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THE ULTRA-VIOLET ABSORPTION SPECTRA

OF CERTAIN

KETIMINES AND THEIR RELATED KETONES

LIST OF CONTENTS

LIST OF FIGURES

ABSTRACT OF THESIS.

1. A review has been made of the preparation and properties of ketimines. At present no similar review exists in the chemical literature.

2. A discussion of the process of absorption, with particular reference to the carbonyl group has been offered. This discussion includes certain effects taking place, hyperconjugation being the most relevant to the thesis.

3. A series of diaryl ketones and ketimines have been prepared and studied by ultra violet spectroscopy; four of these compounds (p-ethyl-, p-iso-propyl-, and p-tert.butyl-benzophenoneimine hydrochlorides, and p-tert.-butyl-benzophenone) have not been prepared before. The preparation and ultra violet absorption study of fenchone and fenchone-imine, have been described.

4. The Hilger Uvispek Spectrophotometer has been described and its limitations, with respect to accuracy, discussed.

PART I

CHAPTER I.

INTRODUCTION - THE PROBLEM AND DEFINITIONS OF TERMS USED.

The Problem.

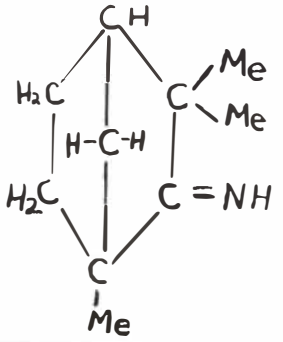
Although relatively many aromatic ketimines have been synthesised, no dialkyl ketimines are known. This appears rather surprising since the oxygen analogue acetone is very stable and has also given rise to a large series of dialkyl ketones. What is more surprising is the fact that alkyl aldimines have been prepared and appear to be more stable than ketimines. These anomalies have therefore given rise to the present investigations.

The manner in which these experiments were carried out, was by use of ultra violet absorption spectroscopy. It was hoped that by investigating different series of these compounds (as shown below), the effects of different substituents could be observed with respect to absorption of light. From this it might be possible to explain the stability of any particular group in terms of tautomerism, resonance, inductive effect, hyperconjugation and other effects which may be correlated with both absorption of light and reactivity.

Fenchone.

If possible it would be advantagious to know the absorption of the C=NH group only. This could be found fairly reliably if the groups R and R' in the system $\begin{matrix} R \\ R' \end{matrix}\!\!>\!C{=}NH$, did not themselves contribute to the absorption in the range in which measurements were made.

Through a search of the literature, it was found that one of the few imines, (if not the only one) to conform with these requirements, was fenchone imine. It can be seen that the system is a single bonded unit displaying no conjugation. Furthermore, the fact that there is no hydrogen on a carbon bonded to the C=NH, will reduce



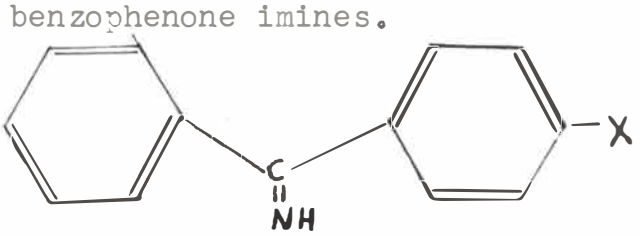
the possibility of $-C-NH_2$ formation. Hence the effect of tautomersion will be negligible, or if present, so small as to fall within the limits of experimental error.

The inductive effect will also be small since the charge transfer produced by the methyl groups is not great and can act in more than one direction. Likewise hyperconjugation is samll since there are no hydrogen atoms on a carbon which is situated α to the -C=NH link and the methyl groups cannot act through a conjugated system.

The fenchone molecule and fenchone-imine are in a state of high strain and it was found impossible to build a molecular model. A portion consisting of the imine group and the neighbouring carbons aarrying methyl groups, was constructed and it was found that although a slight steric hindrance was possible, it would be unlikely.

Diaryl Ketimines.

Next it was decided that a study of diaryl ketimines should be attempted, i.e. benzophenone imine and mono-substituted benzophenone imines.



Different groups were substituted in position X

i.e. X = methyl (CH_3)

= ethyl (C_2H_5)

= iso-propyl ($H-C(CH_3)_2-$)

= tert.-butyl ($CH_3-C(CH_3)_2-$)

The effects of substituting in the para position, will be to eliminate any possibility of steric hindrance. Also there will be no tautomerism present because of the distance of the group X from the double bond. The effects that should be present would therefore be either inductive or hyperconjugation, or both. These effects will tend to increase the conjugation or π

character of the system, and hence increase overall stability. The relative importance of these effects can be seen from a study of the spectra by comparing the shift in wave length of absorption due to introduction of different groups.

This series was investigated and definite shifts were observed. The result of these will be explained more fully under the heading of DISCUSSION AND RESULTS.

Definition of Some Symbols and Terms Used.

λ max: the wave length at which maximum absorption takes place.

ϵ max: the greatest intensity of absorption.

Hyperchrome: a group which causes an increase in the molecular extinction coefficient of an absorption bond.

Hypochrome: a group which causes a decrease in the molecular extinction coefficient of an absorption bond.

Bathochrome: a group which produces a shift of an absorption band toward longer wave lengths.

Hypsochrome: a group which produces a shift of an absorption band toward shorter wave lengths.

Chromophore: a group containing multiple bonds which are fundamentally responsible for the colour of organic substances.

Auxochrome: a group which does not confer colour upon an otherwise colourless substance but does increase the colouring power of a chromophore.

($\pm$ I) Inductive Effect: the permanent polarization arising from the unequal sharing of bonding electrons between two atoms of different nuclear charge, and relayed through a saturated chain of atoms by electrostatic induction. The standard of reference is the electron density at CR_3 in $H\text{-}CR_3$.

($\pm$ M) Mesomeric Effect: this arises from the delocalisation of electron pairs conjugated with an attached, unsaturated system, due to quantum mechanical resonance, present in the ground state of a molecule or ion. It may be symbolised by a curved arrow line ⌒→ which indicates the direction of the electron-pair displacements which must be applied to the single structure in order to obtain a closer approximation to the true electron distribution, e.g. $\ddot{x}\!\rightarrow\! C = \overset{\frown}{C} =$. The mesomeric

effect represents a permanent polarization of the molecule.

(± E) Electromeric Effect: this is a further displacement of electron-pairs of the same type as that which gives rise to the mesomeric effect, but called into play by the electron demands of an external electric field such as that of an attacking reagent.

(± T) Tautomeric Effect: this is the name given to the combined mesomeric and electromeric effects when there is no need to differentiate berween polarization and the polarizability effects.

CHAPTER II.

HISTORICAL AND THEORETICAL REVIEW OF THE PREPARATIONS, PROPERTIES AND REACTIONS OF KETIMINES.

Preparation of Ketimines.

1. The Grignard - Nitrile Synthesis.

The reaction between ethereal solutions of a Grignard reagents and a cyanide was examined originally by Blaise (8) in 1901 (who, however, recorded no yields), and has since been subject to many investigations. The most notable of the earlier workers in this field are Moureu and Mignonac (86, 87) who, between the years 1910 and 1920 published a number of papers dealing with detailed methods of preparations and purifications of the products. This method is at present, the most important and most widely used in the formation of a large and divers variety of diaryl and aryl-alkyl ketimines. In recent years, this method has been used in the preparation of an important series of drugs named amidones (102, 21).

This method has been widely used in the preparation of ketones in which the ketimine is formed as an intermediate only. It is then hydrolysed, often without separation, directly to the ketone.

The general reaction can be described by the use of the following equations.

$$RCN + R'MgX \longrightarrow R - \underset{R'}{C} = N - MgX \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

This reaction mixture is then broken down either by the use of an aqueous solution of ammonium chloride

$$R - \underset{R'}{C} = N - MgX + H_2O \xrightarrow[NH_4Cl]{} R - \underset{R'}{C} = NH + MgX(OH) \ldots\ldots (2)$$

or by the action of dry ammonia (gas or liquid).

$$R - \underset{R'}{C} = N - MgX + NH_3 \longrightarrow R - \underset{R'}{C} = NH + H_2NMgX \ldots\ldots\ldots (2')$$

The formation of the aryl or alkyl magnesium halide has been described by many workers (87, 86, 41). It consists of slowly dropping an ethereal solution of the halide onto

magnesium. The nitrile is then added to this Grignard, and a ketimine complex results, as shown in equation (1). A detailed description of this synthesis can be found on page

Garner and Hellerman[40], in a series of preparations of phenyl-, ethyl-, methyl- β,β,β-triphenylethyl ketimine, state that the alkyl and aralkyl cyanide are known to have an "acidifying" action upon Grignard reagents, as a result of which only low yields of ketimines or ketones may be anticipated. In such reactions acetonitrile affords little or no ketone, and benzyl cyanide gives, after hydrolysis of the reaction mixtures, a low yield (Ca. 3%) of benzylphenyl ketimine, in contrast to the relatively high yields obtained when benzonitriles are employed. These workers used β, β, β-triphenyl-propionitrile and obtained yields as high as 70% in the preparation of phenyl β, β, β-triphenylethyl ketimine hydrochloride.

Similar effects appear to have been noticed by Bruzau[15a] who prepared a series of trisubstituted ketones ($Ph-\overset{CH_3}{\underset{CH_3}{C}}-CO-Ar$). This author, however, noticed that the lower the molecular weight of the nitrile, the higher the yield.

Shriner and Turner[105], on the other hand, claimed that good yields of ketones can be obtained from alkyl cyanides, with almost complete elimination of by products, if an excess of aryl Grignard reagent is used. With acetonitrile and the majority of cyanides, the optimum conditions were four moles of the Grignard reagent to one mole of the nitrile. It is not exactly clear why such a large excess of the Grignard reagent is necessary, but it seems probable that the excess used, converts the nitrile completely to the addition product and hence reducing the tendency of forming polymers of the type $(R.CN)_x$.

It is very probable that because of this tendency of the nitrile to polymerise, and also to form break-down products, that Moureu and Mignonac [87] failed to synthesise any dialkyl ketimines.

Pickard and Vaughan (92) claim that the reaction between the nitrile and Grignard reagent did not take place in ethereal solution during the preparation of a series of alkyl-tolyl, and ditolyl ketimines. Instead, they distilled off the ether after the formation of the Grignard, and then introduced toluene, thus carrying out the nitrile addition at 100° instead of at the boiling point of ether as was done by other workers. Garner and Hellerman (40) reacted their nitrile in a solution of xylene. Contrary to the report of Shriner and Turner (105) is that which Pickard and Vaughan (93) make regarding the ratio of nitrile to halide. They maintain that a ratio varying from 3:1 to 1:1 of aryl halide to aryl nitrile gave no appreciable change in the amount of ketimine, recovered. The probable reason for this is that the aromatic nitriles do not polymerise so easily.

The complex addition compound formed during this addition, has been broken down in a number of ways. The three most important will be outlined below.

(i) Crushed ice and ammonium chloride (86, 40, 33).

This method can be used in the case of ketimines which are fairly resistant to hydrolysis; it is safe to use with diaryl type but not with aralkyl ketimines.

The reaction mixture is poured onto a mixture of crushed ice and ammonium chloride. Hydrolysis takes place according to equation (2), and the ketimine which is formed is extracted with ether.

(ii) Gaseous Ammonia Method (92).

This method has not been used much but is probably the simplest and easiest to work with, since the same apparatus is used throughout the experiment. It consists of bubbling dry ammonia gas through the reaction vessel, which is being stirred for a period of one to two hours. In the present work however, it was found that the reaction mixture tended to solidify, thus reducing the active area of reaction. The formation of the ketimine takes place as an equation (2').

For details see page 61 .

(iii) Liquid Ammonia Method.

This method was developed by Cornell [28], and has been used with great advantage by Smith and Bergstrom [109], who claim to have synthesised very pure samples of benzophenoneimine and by Cloke [22] who synthesised the sensitive ethyl cyclopropyl ketimine. The advantages of this method are that the temperature is kept low, thus reducing to a minimum the tendency to from condensation products, and as in (ii), the products are kept free from moisture thus preventing any hydrolysis to the ketone.

It consists of transferring adducts from the reaction flask to a Dewer flask, and then slowly adding liquid ammonia. The Dewer flask is connected to a lime tower and left standing for twentyfour hours with occasional shaking. Ether is then added and the solids filtered off, after which the ethereal solution is dried and the ketimines distilled. Instead the hydrochloride may be formed by bubbling dry hydrogen chloride into the ethereal solution.

2. Ammonolysis of Ketones.

Although the ketimines are most frequently formed as intermediates in the production of ketones, it often happens that the ketone may be obtained more easily by other means, e.g. Friedel - Crafts synthesis, or may be found in nature. In this case it is possible to carry out a reverse process and synthesize the ketimine from the ketone.

(i) Alcoholic Ammonia.

In 1905 Thomae [113] reported that when a mixture of methyl ethyl ketone with twice its volume of alcohol is saturated with ammonia at intervals during several weeks, being kept in the dark in the meantime, and the product is allowed to evaporate in the air, an amino compound is formed as an oil according to the equation (3).

$$3MeCOEt + 2NH_3 \longrightarrow \begin{matrix} Me \\ Et \end{matrix}\!\!\diagdown\!\!C\!\left(N{=}C\!\!\begin{matrix}\diagup\!\!Me \\ \diagdown\!\!Et\end{matrix}\right)_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

With benzophenone however, he isolated a compound with properties corresponding to benzophenone imine hydrochloride.

$(C_6H_5)_2$ C = NH.HCl .

Thomae was severly criticised by Traube [118], who claimed that the products of the reaction of the dialkyl ketones i.e. acetone, methyl ethyl, methyl propyl and diethyl ketones etc. and ammonia were not imines but rather amines. The methyl ethyl ketone gave CH_2-CMeEt - NH
CO -CHMe - CMeEt

2:3:6 trimethyl- 2:6 diethyl- 4 piperidone and also dimethyl diacetone amine . . . . . COEt-CH_2-CMeEt.NH_2

or . . . . . CCMe-CHMe-CMeEt-NH_2

More recently Rehberg and Henze [97] claimed a 90 to 95% yield of methylphenacyl ketimine from the corresponding ketone, by heating an alcoholic solution of ketone saturated with ammonia in a steel bomb at 110°.

(ii) The Thoria Catalyst Method.

The first serious attempt at synthesis by using ketones and ammonia, was made by Mignonac [79] in 1920. It consisted of packing a glass tube with thorium oxide catalyst (this being prepared by saturation of pumice peas with a solution of catalyst and then evaporating to dryness), which was placed in an electrically heated furnace, held at 300 to 400°. The ketone is evaporated inside the tube, and dry ammonia is passed with the vapour through the combustion tube, and are finally condensed in an ice-salt or dry-ice bath at the end of the tube. The imine is then extracted with ether and separated from the unreacted ketone, by forming the hydrochloride.

This method does not appear to have been used a great deal by other workers. However, in recent years, Castarell [17] claims to have used this method with great success in order to prepare very pure samples of benzophenone imine.

(iii) Liquid Ammonia Method.

The reaction of ammonia on a ketone will lead to the formation of a ketimine and water under suitable conditions.

$$R_2C{=}O + H_2NH \longrightarrow R_2C = NH + H_2O \quad \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

If a dehydrating agent can be used to absorb the moisture, then the yield should be higher. Strain [111] found that anhydrous

aluminium chloride which had been firstly treated with a stream of ammonia, was an excellent catalyst to use. By placing the catalyst, ketone, and ammonia in a sealed tube and heating for four hours at 180°, the imine was formed. The ammonia was then evaporated while the ketone and imine were extracted with ether. By this method, Strain formed a number of ketimines, including acetophenone-,fenchone-, and benzophenone imine hydrochlorides. His yields however were fairly small (20 to 30%) while the analysis he gave for chlorine and nitrogen, showed an error on the calculated results often as great as 9%.

Reid and Lynch (98) in preparing a series of ketimine dyes also used a similar method of synthesis. As catalyst they used chlorides of phosphorous which Strain (111) has claimed too difficult to work with. By this method they obtained a series of amino substituted benzophenone and benzophenone imines in yields varying from 30 to 60%. The reaction mixture in this case was heated in a steel bomb and toluene was used as a solvent.

3. Oxime Conversion.

A number of different attempts have been made in the past to form ketimines by attack on the oxime radical in ketoximes. The first of these methods is a general method and can be applied to a large number of oximes; the others restricted only to certain types.

(i) Catalytic Reduction.

This method was introduced by Mignonac (78) whose intention it was to attempt the preparation of dialkyl ketimines. The advantages are that the reaction takes place according to the following equation.

$$\begin{matrix} R \\ R' \end{matrix}\!\!>\!C = NOH + H_2 \longrightarrow \begin{matrix} R \\ R' \end{matrix}\!\!>\!C = NH + H_2O \quad \ldots\ldots\ldots\ldots\ldots(5)$$

It consists of suspending a finely powdered nickel catalyst (which had been formed by the reduction of the oxide at 300°) into a solution of the oxime in absolute alcohol. Hydrogen is now introduced at approximately atmospheric pressure. The reaction flask is connected to a pressure gauge, and shaken

vigorously at room temperature until the theoretical volume has been absorbed (one mole of H_2 to one mole of oxime). The reaction is now stopped, the catalyst filtered, and the product separated by fractional distillation in vacuum.

There appears to be a danger of reduction to the amine in this method, and it has often been used for the synthesis of amines directly [70]. Another difficulty is the formation of water which Mignonac [78] appears to have neglected altogether. Some form of dehydrating agent as used in the ammonolysis of ketones ([111, 98]) would probably increase the yields which were stated as being smaller than 50%.

(ii) Action of Heat Upon Oximes.

Lachman [63] showed that when benzophenone oxime was heated, the rearrangement to benzanilide postulated by Beckmann did not occur. On heating this compound in air he found that decomposition began at about 185° and the products formed were benzophenone and nitric acid. When the oxime was heated in an inert gas or vacuum, the products were mainly benzophenone and benzophenone imine.

$$2(C_6H_5)_2\ C = NOH \longrightarrow (C_6H_5)_2\ C{=}O + (C_6H_5)_2C{=}NH + (NOH) \quad ....(6)$$

The NOH radical broke down to yield nitrogen, nitric oxides and water. The water thus produced reacted with the imine forming the ketone. The product in the form of a liquid was easily distilled yielding about 40% benzophenone imine.

(iii) Action of Nitrous Acid and Ammonia.

Mahla and Tiemann [71] as well as other earlier workers (see APPENDIX I for details) have described how ketones amongst the terpenes particularly fenchone and camphor can be converted to imines by the use of oximes.

An ethereal solution of oxime is shaken vigorously for some hours with a nitrous acid solution. A nitro compound is presumably formed which can be isolated by evaporating the ether. This compound is then shaken with a 25% aqueous solution with the result that an oil separates. This is extracted with ether, the solution dried, and the ketimine distilled under vacuum.

(iv) Action of Chlorostannic Acid.

This preparation is very doubtful. Sonn and Meyer (110) claim that they obtained a double tin salt of acetone imine $\left[(CH_3)_2 C = NH\right]_2 H_2SnCl_6$, by mixing an ethereal solution of acetoxime (one mole) with chlorostannic acid (three moles) and leaving the mixture standing for four weeks, when large transparent crystals formed. This experiment was repeated by the present investigator but no crystals formed after many months, even when the side of the containers were scratched and left standing at -20° for some days.

4. Houben - Hoesch Synthesis.

(i) The Hoesch synthesis for hydroxy- and alkoxy phenyl alkyl ketimines and ketones (52).

The method was first proposed by Hoesch in 1915 as a method for the preparation of phenolic ketones for which the Friedel - Crafts and other methods were inadequate. It consists of passing hydrogen chloride through an equimolecular ethereal solution of phenol or phenyl ester and nitrile with powdered fused zinc chloride. A ketimine hydrochloride is formed which on treatment with water is hydrolysed to the ketone.

An example of this, is a mixture of resorcinol and acetonitrile in ethereal solution in the presence of zinc chloride. When treated with hydrogen chloride, a ketimine hydrochloride begins to separate in half an hour, and treatment of this product with water converts it into resacetophenone, giving a yield 70% of the theoretical. The monomethyl ether of resorcinol under analogous treatment gives paenol (6-hydroxy-4-methoxy-acetophenone) together with isopaenol (4-hydroxy-2methoxy-acetophenone). In each case the ketimine hydrochloride could be separated by filtering and then dissolving in chloroform or alcohol, from which it could be reprecipitated by ether.

(ii) The Houben Extension.

Houben (53) used the above method for the nuclear condensation of phenols and phenolic ethers with nitriles, which yielded phenol and phenol ether ketimines and ketones. The yields

he reported were very small however, and he found that by using ferric chloride in place of zinc chloride he could increase these yields.

This method was further extended by Houben (54-56) and Fischer to the formation of halogen, nitro, amino aryl ketones and ketimines. These authors found that by using anhydrous aluminium chloride as catalyst and chlorobenzene as solvent, instead of ether, they could obtain high yields. They also found it was possible to use a halogen substituted nitrile. The reaction mixture was decomposed with alkali hydroxide or with a large amount of crushed ice, which lowered the temperature to such an extent that much hydrolysis was prevented. This method gave an 80% yield of trichloro-methyl p-tolyl ketimine hydrochloride, by using toluene, trichloro-acetonitrile (CCl_3CN), aluminium chloride and chlorobenzene, while hydrogen chloride was bubbled through.

5. Ammonolysis of Dichloro Aryl Compounds.

These methods are not economical since they require firstly the preparation of the starting materials which is often difficult, the yields are low and in the case of the first preparation, a large excess of urethane is required.

(i) Hantzch and Kraft (44) were probably the first to prepare a ketimine when they formed benzophenone imine hydrochloride, and then isolated the free base. The reaction was carried out by heating diphenyldichloromethane (benzophenone chloride) with a large excess of urethane.

$$(C_6H_5)_2CCl_2 + H_2NCOOC_2H_5 \longrightarrow (C_6H_5)_2C{=}NH.HCl + CO_2 + C_2H_5Cl \quad ..(7)$$

Moore(80) prepared a sample of benzophenone imine hydrobromide by passing ammonia through a solution of diphenyldibromomethane in chloroform. The product was obtained as large colourless crystals.

$$(C_6H_5)_2CBr_2 + NH_3 \longrightarrow (C_6H_5)_2C{=}NH.HBr + HBr \quad ..... \quad (8)$$

There are probably some other minor methods of preparation, but these at present are of limited importance. An example is a recent preparation of a number of picolyl

and pyridyl ketimines [132] . The reaction of 2 picolyllithium $C_5H_4NCH_2Li$ with a nitrile RCN in alcohol yields the corresponding ketimines which may be readily hydrolysed to ketones.

Since ketimines are at present important mainly as intermediates in the production of ketones, methods 1. and 4. have the widest application.

Properties of Ketimines and Their Salts.

(i) Physical Properties.

The ketimines exist either as high boiling oils or low melting solids. The liquids are either colourless or else a pale yellow with a pungent smell. The solids are either white or yellow and melt with darkening of colour. The density of the liquid is about 0.90 to 1.0 at 20° and the refractive index is in the range of 1.5 to 1.6. The salts of the ketimines may be white as in the case of hydrochlorides or yellow as in the case of picrates. They melt usually at a temperature greater than 180°. The hydrochlorides which are the most commonly used salts, sublime very readily, some doing so to the exclusion of melting. Others sublime very little but have distinct melting points. Prior to melting, the colour tends to change to a dark brown.

(ii) Chemical Properties.

The ketimines are weak bases and will form salts with weak acids e.g. picric, benzoic; with strong acids they are hydrolysed to the ketones.

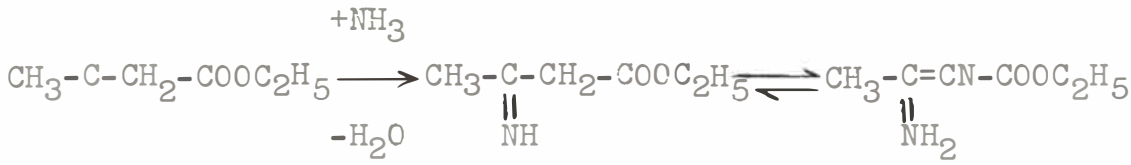
(a) Ketimine - Enamine Tautomerism.

This form of tautomerism was suggested by the early work of Collie [25] and particularly J.F. Thorpe [81] and co-workers, who from 1900 ti 1910 published numerous papers on tautomerism in imino compounds. An example can be given from the work of Ruhemann and Watson [100], 1904 who found that when alcoholic ammonia reacted with α, β-dibromobenzylacetophenone they obtained a product to which they assigned the formula

$$C_6H_5 - \underset{\underset{NH_2}{|}}{C} = CHCOC_6H_5 \quad \text{or} \quad C_6H_5 - \underset{\underset{NH}{\|}}{C} - CH_2COC_6H_5$$

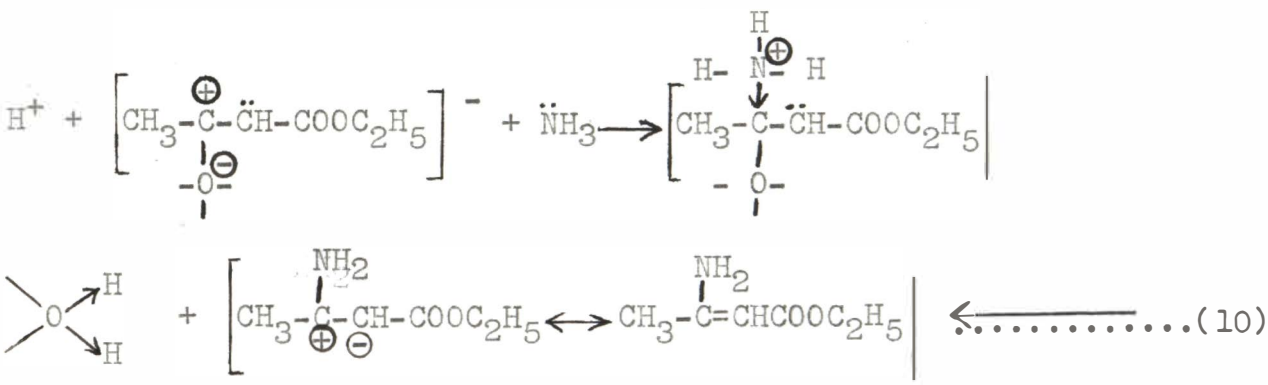
In more recent years a similar study has been made on tautomerism as found in acetoacetic ester.

Henecka [49] has recently given a review of the work carried out on this subject. He claims that if ammonia react with acetoacetic ester, a ketimine is formed while water breaks off. The ketimine is ethyl imino-buterate (x) or its tautomer ethyl amino-crotonate (y). This reaction presumably takes place



(x) (y)....(9)

in such a way that the polerized end of the enolic formula adds one mole of ammonia, whereupon the resultant then becomes stabilised. This proceeds with release of water and reformation of conjugation.



Similarly, as the keto-enol tautomerism takes place in ketones, it should be possible to have imine-enamine tautomerism taking place between ketimines and amines as shown by (x) and (y). Since the tautomers of enamine do not have any reaction with ferric chloride, and furthermore since there is no method of identifying enamines by titration with bromine as used to give quantitative measurements of enol formation, it is obvious that little is known of the imine-enamine tautomerism that exists in ethyl imino-buterate. From purely chemical considerations, however, it is very likely that the enamine form i.e. ethyl amino-crotonate preponderates in the equilibrium mixture. Similar compounds are obtained by the action of mono and dialkyl amines on acetoacetic ester instead of ammonia and give

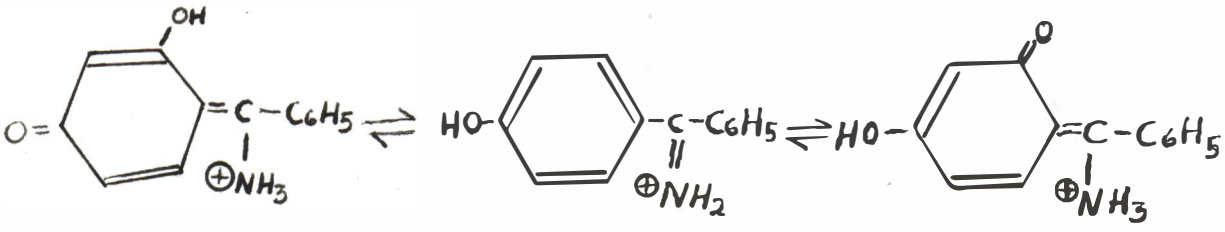
It is found that these compounds behave as primary amines. They are very difficult to hydrolyse with water, while ketimines are very sensitive to hydrolysis.

Von Auwers [2] by a study molar refraction and absorption spectra, came to the conclusion that when ketimine-enamine tautomerism is possible, compounds in a molten or dissolved state will exist almost exclusively as enamines. It is only in cases where the enamine formation is impossible that compounds will exist as ketimines. These results were confirmed more recently by Glickman and Cope [43] who showed that due to the formation of a conjugated system in enamines, the absorption of light took place at a longer wave length. While in keto-enol compounds the equilibrium depends mainly on the type of molecule and on outer conditions [130], such influences appear to be negligible with ketimine-enamine substances. The former would require a smaller energy for orientation since the mobility of the protons on nitrogen is smaller than oxygen i.e. the nitrogen atom tending to be more unsaturated than the oxygen atom and therefore holding the maximum hydrogen corresponding to enamine formation.

Furthermore, enamines are favoured since here, as with enol forms of β dicarbonyl compounds chelation can take place with resonance between the most favourable energy states. This will lead to pseudo-aromatic structure and hence an increase in stability.

Culbertson [33] demonstrates a tautomerism which can take place in polyhydric diphenyl compounds, which he claims to be surprisingly stable towards hydrolysis. It is probable that

this occurs between a benzenoid-imine and quinonoid-amine structure, as here illustrated for 2, 4-dihydroxydiphenyl ketimine salt ion. It may be possible for the tautomerism to



(A) (B)

p-quinonoid-amine benzenoid-imine o-quinonoid-amine

go from one quinonoid-amine structure to the other by shift of the phenolic "H". Although this may not be probable, it would account for the stability to hydrolysis. Culbertson (op. cit.) mentions that in studying a series of dihydroxy diphenyl compounds he observed from rates of hydrolysis, colours of free bases and solubility in various solvents, that such tautomerism is possible.

Closely related to these ketimines is the dye auramine. The dual behaviour of this compound has suggested a tautomeric equilibrium for it; the first of these is a benzenoid-imine

$$(CH_3)_2{}^{+}NH\text{-}C_6H_4\text{-}C(=NH)\text{-}C_6H_4N(CH_3)_2 \rightleftharpoons (CH_3)_2{}^{+}N=C_6H_4=C(-NH_2)C_6H_4N(CH_3)_2$$

(ketimine) and the second a quinonoid-amine structure. The fact that auramine undergoes a measurable, though slow, hydrolysis to Michler's ketone indicates that the benzenoid-imine structure exists.

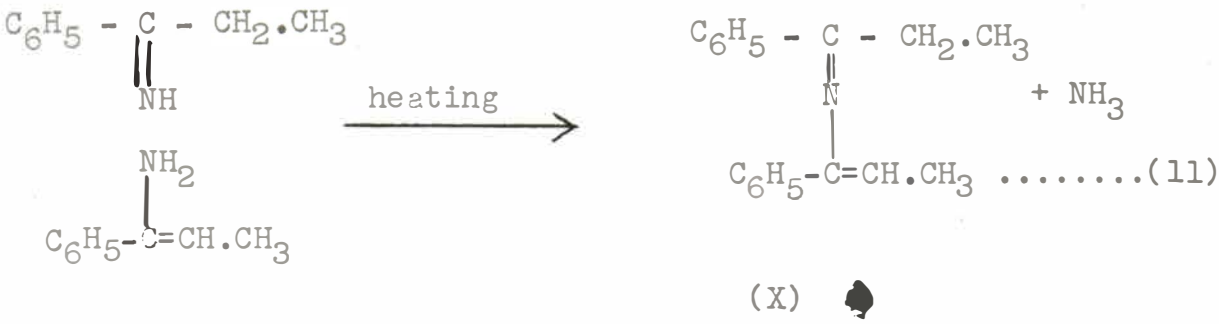
Moureu and Mignonac [87] found that when a ketimine was heated strongly, a portion of it was converted to a compound they named a ketiso-ketimine. The formation was due to the possibility of tautomerism by compounds having a labile hydrogen on the carbon next to the carbimino group.

$$C_6H_5\text{-}\underset{\underset{NH}{|}}{C}\text{-}\ CH_2\text{-}CH_3 \rightleftharpoons C_6H_5\ \text{-}\underset{\underset{NH_2}{|}}{C}\ =CH.CH_3$$

Ketimine Form Enamine Form.

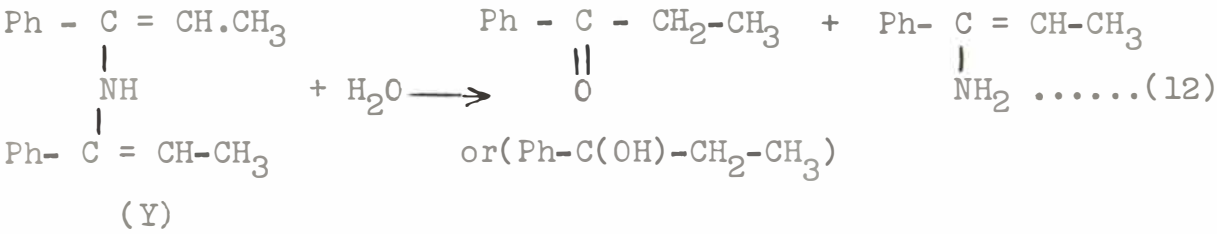
The ketiso-ketimine was then formed by the combination of these

two forms with the breaking off of ammonia;



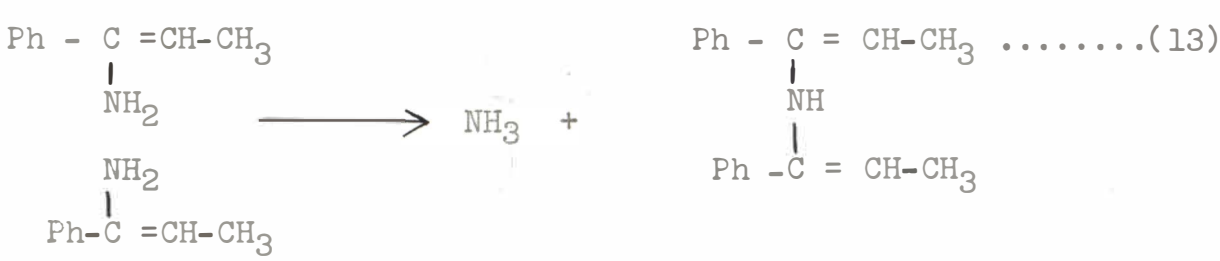
(X)

It is possible that this ketiso-ketimine (X) could have another structure (Y). Both these structures give identical products on hydrolysis.



(Y)

Moureu and Mignonac (loc. cit.) showed that the formula (X) was clearly predominant and probably the only form, since by the action of Grignard on this substance they obtained products showing there was no hydrogen attached to the nitrogen. The formula (Y) could however be obtained by heating two moles of an amine.



(b) Hydrolysis.

Ketimines are very sensitive to the attack of water and acids which will hydrolyse most of them to the respective ketones (see page 43 for equation). Moureu and Mignonac (87) stated that the salts were hydrolysed with more ease than the free bases, but this app ears to be more of a qualitative observation than a result obtained from planned experiments.

At the present time very little quantitative work has been carried out on these compounds; techniques are limited in use, and probably give good approximations only. They depend on the relative solubilities of the reactants or products in different solvents. Culbertson (33) extracted the ketones

formed at different intervals, with benzene, and then weighed the product after evaporation of the solvents. This of course applies to slow rates of hydrolysis and to ketones having low volatility.

It has generally been observed that decrease in temperature will result in a marked decrease in the rate of hydrolysis. In the formation of the diaryl type of ketimines and other more stable ones, the reaction mixture is decomposed by ice. A point of interest arises, however, from the work carried out independently by Culbertson (op. cit.) on dihydroxy- and dimethoxy-diphenyl ketimine salts, and Cloke [22-24] on cyclopropyl ketimine salts. Both these workers claim that the rate of hydrolysis decreased with increase of pH at certain concentrations. The former working between a pH of 3.5 and 5.6 obtained a decrease insufficient however to alter greatly the order of magnitude of comparative values. The following table from Cloke's [22] work illustrates the point well.

TABLE I

VARIATION OF HYDROLYSIS RATE WITH pH

Cyclopropyl ketimine hydrochloride	HCl.N	Av. k. min^{-1} at 0°
Ethyl	0.05	0.00284
Ethyl	.20	.00118
Phenyl	.01	.00747
Phenyl	.05	.00435
Phenyl	.20	.00189

Reactions of Ketimines.

Smith and Bergstrom [109] have outlined a series of interesting reactions which the ketimines follow. They have taken benzophenone imine as a typical example of a ketimine. (i) They have found that this imine reacts vigorously with phenylhydrazine, hydroxylamine in liquid ammonia, and aniline to give benzophenone hydrazone, -oxime, and -anil respectively.

$(C_6H_5)_2C{=}NH + C_6H_5.NH.NH_2 \longrightarrow (C_6H_5)C{=}N.NH.C_6H_5 + NH_3$ ..(14)

$(C_6H_5)_2C{=}NH + H_2NOH \longrightarrow (C_6H_5)C{=}NOH + NH_3$ .....(15)

$(C_6H_5)_2C{=}NH + C_6H_5NH_2 \longrightarrow (C_6H_5)C{=}NC_6H_5 + NH_3$ .....(16)

Bruzau [15a] points out that the yield of oxime obtained this way is higher than by using the ketone.

(ii) Benzophenone imine readily adds hydrogen cyanide in alcoholic solution;

$(C_6H_5)_2C{=}NH + HCN \longrightarrow (C_6H_5)C(NH_2){-}CN$..... ..(17)

Phenyl isocyanide reacts with benzophenone imine producing benzohydrylidene phenyl-urea, which is easily hydrolysed to phenyl-urea and benzophenone.

$(C_6H_5)_2C{=}NH + C_6H_5NCO \longrightarrow C_6H_5NHCON{=}C(C_6H_5)_2$ .....(18)

$C_6H_5NHCON{=}C(C_6H_5)_2 \xrightarrow{H_2O} C_6H_5NHCONH_2 + (C_6H_5)_2C{=}O$

(iii) With potassium and sodium amides in liquid ammonia, benzophenone imine forms lighly coloured and very soluble salts.

$(C_6H_5)_2C{=}NH + NaNH_2 \longrightarrow (C_6H_5)_2C{=}N.Na + NH_3$ .....(19)

$(C_6H_5)_2C{=}NH + 2KNH_2 \longrightarrow C(C_6H_5)_2(NHK)_2 + NH_3$ .....(20)

(iv) Reductions. Pickard and Vaughan [92] have shown that it is possible to reduce the imines quantitatively to the amine with hydrogen, at room temperature and atmospheric pressure in alcoholic solution, by using a pre-reduced Adams platinum catalyst.

(v) Houben and Fischer [57] found that by shaking an ethereal solution of ketimine with powdered potassium hydroxide or calcium oxide they obtained a nitrile and chloroform.

$p\text{-}Me.C_6H_4C(=NH) - CCl_3 \xrightarrow{KOH} p\text{-}MeC_6H_4CN + CHCl_3$ ..... (21)

(vi) Dimerization. Two recent papers [94, 50] have shown that when a Grignard reagent reacts with an unsaturated nitrile, the

the product will be a ketimine dimer. An example is cinnamonitrile which yielded a styryl ketimine hydrochloride. The structures appear to be of a bridged pyrimidine type.

CHAPTER III

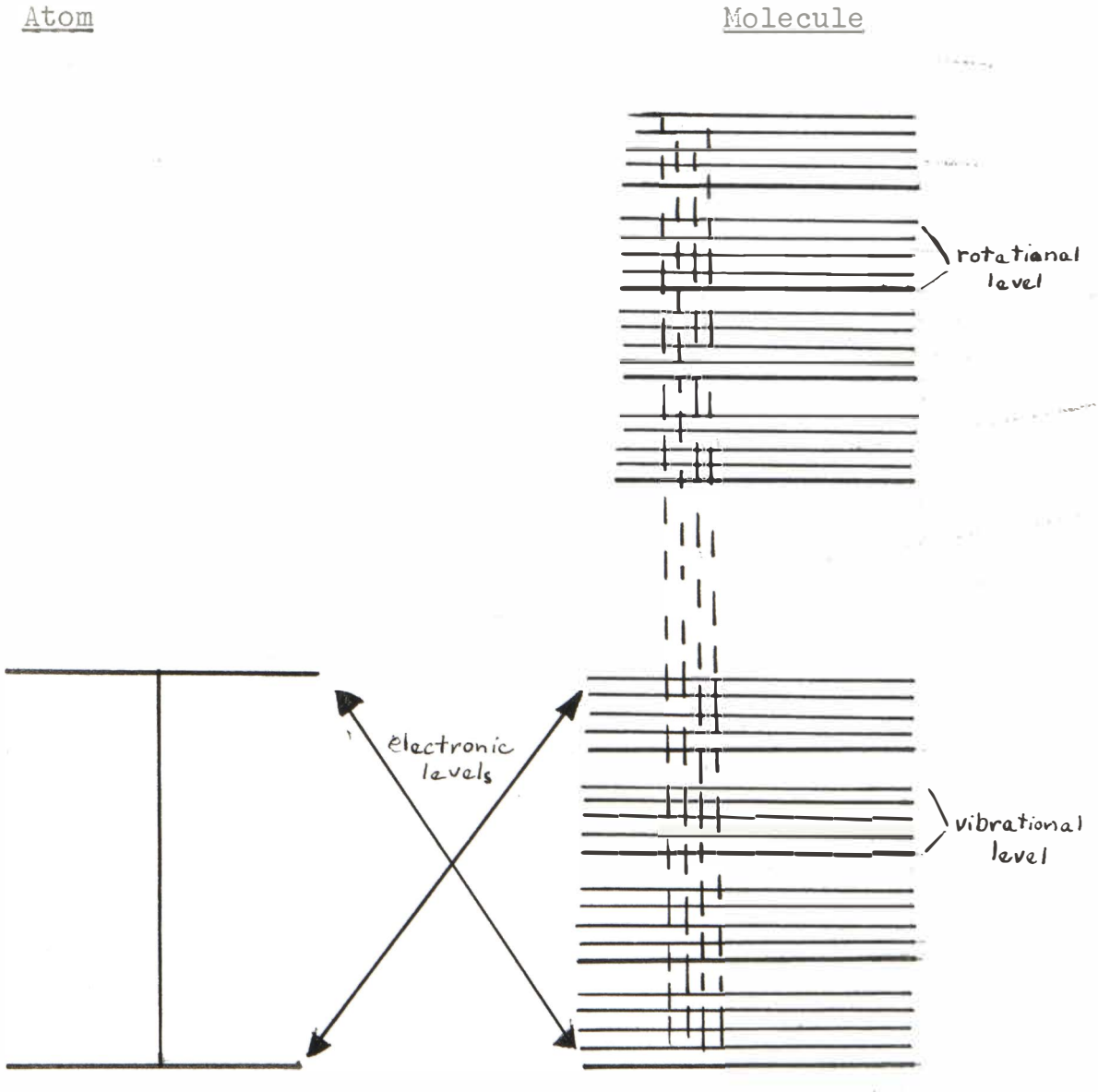
HISTORICAL AND THEORETICAL REVIEW OF THE LIGHT ABSORPTION PROCESS.

(i) Nature and Origin of Ultra Violet Absorption Spectroscopy.

As in the case of atoms, the absorption spectra of molecules are to be attributed to transitions, upon absorption of energy in the form of radiation, from states of low energy content to those of high energy content. In contrast to sharp-line atomic spectra, however, molecular spectra are broad, that is, spread over a wide range of wave-lengths. The difference may be understood readily by reference to a diagram (Fig. 1.) of the energy levels in the two species.

Figure 1

ENERGY LEVELS.



In atoms, separate levels arise from the different energies accompanying various distributions of the electrons, there is associated with any given electronic arrangement various possible modes of vibration between the atoms, each with a definite difference in energy, and for each mode of vibration there is also a number of possible modes of rotation accompanied by differences in energy. Rotation energy differences are small in comparison with vibrational energies and the latter, in turn are of a lower order of magnitude relative to differences in energy of electronic states. As a result, a complex energy-level diagram is obtained from molecules, and many transitions are possible in which the differences in energy are very close as is indicated in Fig.1. According to the Bohr relation the frequency (ν) of the light absorbed is directly proportional to the difference in energy, $E_2 - E_1$, between the two states involved in the transition i.e. $h\nu = E_2 - E_1$. Where h is Plancks constant. Consequently, with molecules, large numbers of lines in close proximity are observed. In most cases, these lines are so close they cannot be distinguished with an ordinary spectrograph and hence appear as a broad region of absorption called a band.

Absorption in the near ultra violet (2000 - 4000 Å) corresponds to energy increases of 70 - 140 k. cals. per mole, intermediate between those required for the photo-ionization of single covalent bonds and those required for vibrational or rotational transitions. Quanta of this magnitude are involved in the displacement of "mobile electrons" (64).

The two most important types of mobile electrons found in organic compounds are the "unsaturation" electrons of multiple bonds and the unpaired or lone electrons of free radicals.

Whereas the wave-length of light absorbed is determined by the energy of the transition involved, the intensity of absorption is related to the probability of that transition. Maxima in the extinction curves correspond to the most probable transitions, and the absorption of a counpound is often expressed in terms of the wave-length and extinction coefficient

of the maxima (λ max, ϵ max). The intensity of absorption can also be expressed in terms of area ($\int \epsilon d\lambda$) under the extinction curve. The highest possible value of ϵ can be calculated from the cross-sectional area of the molecule [13] and is of the order of $10^5 - 10^6$ for simple molecules. The values of ϵ max actually met with, are normally smaller than this ($1 - 10^5$) indicating that the effective absorbing area ("Chromophore area") is usually smaller than that of the molecule, and the probability of the transitions less than unity.

The importance of the intensity as well as the wave-length of maximum absorption was emphasised by Chako [20]. He pointed out that a number of the bands which were responsible for the colour of organic compounds were relatively weak, and by applying the classical theory of light absorption process, he was able to calculate a measure of the intensity of absorption in the so-called oscillator strength. This theory was developed mainly by Chako and Forster [38], and a number of reviews [82, 38, 88, 69] have since described its derivation in detail.

(ii) The Classical Theory of Light Absorption.

This theory is based upon Maxwell's electromagnetic theory and the concept of electrons. In order to investigate the interaction of radiation with matter, some hypothesis as to the structure of matter has to be made. The concept of normal dispersion (increase of refractive index with increase in velocity of light) is used, and the analysis is carried out by assuming that the electrons are subject to a "damping force", proportional to their velocities. An expression is thus obtained for a substance in the gaseous state.

$$2n^2K = \frac{e^2N'}{\pi m} \frac{f_j \gamma_j \nu^2}{(\nu_j^2 - \nu^2)^2 + \gamma_j \nu^2} \qquad \text{---------- (1)}$$

Where n = refractive index of medium

e = charge on electron

ν_j = frequency of maximum absorption

γ_j = a quantity measuring damping and responsible for width of bands

f_j = measures the strength in classical theory. It is the number of electrons per molecule producing the band

N' = molecules per c.c.

K is determined by the ratio of the energy of the wave after having traversed a distance Z in the medium, to its value on entering the medium. This treatment leads to

$$I = I_0 e^{2\omega K n z/u} \qquad \text{---------- (2)}$$

u = velocity of light

ω = angular velocity

This is for a gaseous state; since K is proportional to N', (2) may be expressed as

$$I = I_0 e^{-\epsilon c d} \qquad \text{---------- (3)}$$

ϵ = extinction coefficient (a measure of the light absorbed)

c = concentration of the medium

d = distance through which the light has travelled.

It now follows from (1), (2), and (3) that

$$\epsilon' = \frac{2e^2N}{u^2mn} \frac{f_j \gamma_j \nu^2}{(\nu_j^2 - \nu^2) + \gamma_j \nu^2} \qquad \text{---------- (4)}$$

N = avagadros number

The plot of ϵ against ν gives a parabolic curve in which ϵ reaches a maxima when $\nu = \nu_j$. The substance is then said to have an absorption band at γ_j.

In addition it is possible to find the area under the curve if it is sufficiently narrow by applying the following relation,

$$\int \epsilon d\nu = \frac{\pi e^2 N f_j}{u^2 m n} \qquad \text{---------- (5)}$$

Now from (4) it follows that

$$\epsilon_{max} = \frac{2e^2 N f_j \times 10^{-3}}{u^2 m \gamma_j} (m=1) \qquad \text{---------- (6)}$$

or by using (5)

$$\gamma_j \epsilon_{max.} = \frac{2}{\pi} \int \epsilon d\nu \qquad \text{---------- (7)}$$

If is constant throughout the band

$$\Delta\nu = 2\gamma_j \qquad \text{---------- (8)}$$

Where $\Delta\nu$ is the distance between the points at which $\epsilon = \frac{1}{2}\epsilon$ max. The "damping constant" γ_j is equal to the half width of the band. Although Chako [20] found γ_j from both (6) and (7) he could not interpret this constant with regard to the chemical constitution of the substance or the nature of the solvent.

Equation (6) allows an estimate to be made of the magnitude ϵ max. If it is assumed that $f_j = 1$ i.e. there is one electron per molecule concerned in the absorption process, and $\gamma_j \sim 2000\ cm^{-1}$, then substitution shows ϵ max to be of the order 100,000.

To determine the f value of a band, the method usually employed is to measure the area under the curve obtained by plotting ϵ as a function of ν; f can then be calculated from (5), allowance being made for the change of base of the logarithms. Thus

$$f = 4{\cdot}31 \times 10^{-9} \int \epsilon \, d\nu \qquad \text{---------- (9)}$$

The old quantum theory provides an explanation of the low values of f ($\sim$ 0.0001) which are sometimes observed for molecules. On the old classical theory, the explanation appears too simplified and erroneous, namely that only one in ten thousand molecules was of a kind capable of absorption. The old quantum theory interprets f as the probability of transition for a given molecule. This view makes possible numbers, but no further information as to their magnitude could be obtained, apart from the fact that $\sum_j f_j$ was equal to the total number of electrons in the molecule. On the basis of the dispersion theory, the f_j are known as oscillator strengths.

(iii) The Quasi-Classical Theory.

With the advent of the mathematical treatments of electron behaviour derived by Schrodinger in his formulation of the noted equation, spectroscopy took a new turn.

The molecules were described by a potential energy well, [42] in which the atoms could vibrate in a simple harmonic motion. By considering a displacement x and a restoring force k, it was

possible to show that for a diatomic molecule with reduced mass W

$$\frac{1}{\nu_0} = 2\pi\sqrt{\frac{W}{k}} \qquad \text{---------- (10)}$$

and since $E = (v + \frac{1}{2})h\nu_0$ ---------- (11)

$$\therefore E = \frac{h}{2\pi}\sqrt{\frac{k}{W}}\left(v + \frac{1}{2}\right) \qquad \text{---------- (12)}$$

Where v is the quantum number describing the vibrational state in which the molecule exists.

This concept of a potential well has been further extended by Frank and Condon [42, 115, 26] who gave a quantum mechanical treatment of electronic transitions which would take place in the transition of an electron from one quantal state to a higher one. Depending on the transition, it was possible to find the energy required, and hence the frequency of absorption. This treatment is at present however, confined to very simple diatomic molecules.

The concept of the harmonic oscillator was applied by Lewis and Calvin [65] to the formulation of what they called an electronic oscillator. In this case v became the electronic quantum number and W the mass of the effective electrons. If E_0 and E_1 are the energies of the ground and first excited states, respectively, then the frequency of flight causing this transition will be

$$E_1 - E_0 \left(\tfrac{3}{2} - \tfrac{1}{2}\right)h\nu_0 = h\nu_0 \qquad \text{---------- (13)}$$

and for its wave-length

$$\lambda = \frac{u}{\nu_0} = 2\pi u\sqrt{\frac{W}{k}} \qquad \text{---------- (14)}$$

This means that the chromophoric power of different bonds will vary inversely with their restoring force constants k. Single bonds with a large k will absorb in the far ultra violet [124]. Lewis and Calvin postulated that resonance takes place in single bonds with the formation of ionic structures e.g. for ethane they postulated three dynamic structures.

$H_3\overset{+}{C}\ :\bar{C}H_3 \qquad H_3C - CH_3 \qquad H_3\bar{C}:\ \overset{+}{C}H_3$

For double bonds, these authors consider that (a) both bonds

are equivalent and (b) the lone electron pair which exist on such atoms as oxygen, nitrogen, sulphur, play no part in the mechanism of absorption, which they describe as being inherent in the double bond. Both these fundamental assumptions appear to be incorrect. Coulson [29] has recently shown by quantum mechanical calculations (valence bond method) that in ethylenic type stucture, trigonal hybridization has taken place leading to a σ bond on which is superimposed a π bond. The second assumption (b), is likewise unsound. In a series of experiments carried out on aryl substituted aliphatic compounds Kharkharov [59] came to the conclusion that both lone pair electrons and free radicals are important in the process of light absorption. Bowen [11] and other more recent writers have likewise illustrated the important part played by lone electron pairs through the molecular orbital treatment of quantum mechanics. These facts do not however cloud the valuable contributions that Lewis and Calvin have given to the qualitative descriptions of chemical constitution with respect to light absorption. The last named authors considered a series of double bonds

$$\rangle C = C \langle \qquad \rangle C = N - \qquad \rangle C = O \qquad - N = N - \qquad \rangle C = S$$

arranged in order of decreasing force constants by the following arguments. Simple compounds containing a carbon-carbon double bond absorb in the region of 2000Å; those having a C=O bond at about 2800Å, while absorption characteristic of the azo-group lies at about 3500Å. Ferguson [37] lists a series of such compounds with their maximum absorptions.

	$H_2C=CH_2$	$(CH_3)_2C=NCH_3$	$(CH_3)_2C=O$
max =	2000Å	2300Å	2800Å
	$CH_3N=NCH_3$	$(CH_3)_2C=S$	$C_{11}H_9N=O$
max =	3470Å	4000Å	6650Å

The order of increasing chromophoric power for these double bonds is given due to the increased strain within the bonds [65, 59, 37]. With increasing strain, there results a less stable ground state, causing a smaller difference in the potential energies of the ground and first excited states, and hence an absorption of light (excitation) of longer wave-lengths.

Lewis and Calvin consider the double bonded ground as a single oscillating unit. It is possible to have a number of different electronic structures (see page 28) in which case a dipole is formed, and it is the polarizability of the molecule that has direct connection with the absorbing process. (Brooker and co-workers [14] have shown by their work on cyanine and similar dyes, that the more deeply coloured substances have larger dipole moments). This could be well explained by considering a "nearly-linear" conjugated system such as the polyenes. If as a first approximation the effect of the end groups is neglected, these systems can be represented by $R\text{-}(CH{=}CH)_n\text{-}R$ the extreme structures being

$$R\text{-}\overset{+}{C}H\text{-}(CH{=}CH)_{n-1}\text{-}\overset{-}{\underset{\cdot\cdot}{C}}H\text{-}R \quad \text{and} \quad R\text{-}\overset{-}{\underset{\cdot\cdot}{C}}H\text{-}(CH{=}CH)_{n-1}\text{-}\overset{+}{C}H\text{-}R$$

The normal state of the molecule will be non-polar. However, in the presence of an electric field of strength V, a moment (μ) will be induced in each $\rangle CH{=}CH\langle$ unit given by

$$\mu = ex = \alpha V \qquad \text{---------(15)}$$

x being the displacement of the charge and α the polarizability of the molecule. When the electrons are displaced, the electric force acting on them must be balanced by the restoring forces. Thus

$$eE = kx \qquad \text{---------(16)}$$

From (15) and (16) it follows that the force constant is given by

$$k = e^2/\alpha \qquad \text{---------(17)}$$

If the molecule is now placed in the field of a light wave whose wave-length is long compared with the dimensions of a molecule, individual oscillations are set up in the units of the chain, the displacements being the same for each unit. On the assumption that in the excited state of the molecule, the oscillations are of the same character as the induced oscillations discussed above a relationship similar to (10) can be obtained.

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{w_n}} \qquad \text{---------(18)}$$

where n is the number of units in the chain;

hence

$$\lambda = 2\pi u\sqrt{\frac{w_n}{k}} \qquad \text{---------(19)}$$

by squaring both sides $\lambda^2 = \frac{4\pi^2 \mu W \cdot n}{k}$ ---------- (20)

or $\lambda^2 = k'n$ ---------- (20a)

This predicts a linear relationship between λ^2 and the number of units in the chain. Hence the plot of λ^2 against n should give a straight line of the form $\lambda^2 = A + Bn$.

Another system of compounds studied were the carbocyanines the essential structure being

$\rangle \overset{+}{N}=CH-(CH=CH)_n-N\langle$ and $\rangle N-(CH=CH)_n-CH=\overset{+}{N}\langle$

In this case, the charge is distributed through the whole molecule. The relationship derived between max and n was

$$\lambda = k''n \qquad \text{---------- (21)}$$

Although these calculations are only very good approximations, since end groups are not considered, Ferguson [37] tabulates a large number of these compounds in which theory and experiment are in excellent agreement.

(iv) The Quantum Theory of Light Absorption.

With the conception of the wave equation by Schrodinger in 1927, there arose a system of mathematical enquiry into the exact constitution of atoms and molecules. This was originally developed by Heisenberg, Heitler [48] and London. Since then it has been extended by Pauling [91], Mulliken [88], Sklar [107], Lennard-Jones [64], Coulson [30, 29], Walsh [125, 124, 126] and many other workers from the study of simple diatomic molecules to the more complicated organic systems. This quantum mechanical study is based on the hypothesis that the electrons exist as clouds of charges, having an energy E termed an "eigenvalue" and a wave function ψ termed an "eigenfunction" such that ψ^2 is the intensity or probability of finding an electron in any particular spot. By contributing to each electron its own particular eigenfunction, it is possible to set up a number of theoretical configurations for any particular system.

At the present time there exist two major theoretical approaches to the problem, namely the Valence bond (V.B.) and the Molecular orbital (M.O.) methods. Both of these methods,

when generalised so as to apply to complex organic molecules, suffer from limitations, the V.B. method on account of its neglect of ionic structures, the M.O. method because of its treatment in terms of a single electron, with consequent neglect of interelectronic interaction. In the past (prior to 1945) these methods were so much at variance that opposite conclusions were often drawn by the different approaches. An example is that of cis and trans butadiene [69]. In recent years however, many of the limitations have been noticed, and by less rigorous applications the results have been made to agree closely [31]. As many excellent reviews have been written by the above authors and others [34, 62], it is the intention of the present investigator to use these methods in giving a brief description of their present application to the study of electronic absorption spectroscopy.

Some Quantum - Mechanical Aspects of the Carbonyl Group.

By application of the molecular orbital method, McMurray [70] was able to offer a good explanation of the transitions taking place during the absorption of ultra violet radiation. A more qualitative description has been given by Bowen [10, 11] and Walsh [125], a summary of their results being given below.

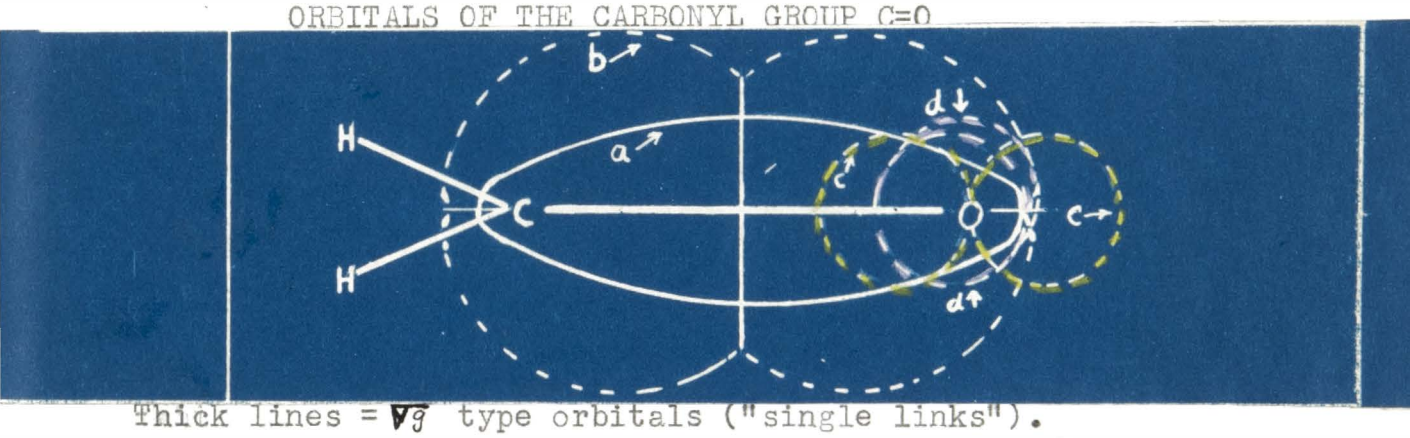
Aldehydes and ketones have a strong absorption region at 1900A corresponding to the absorption of ethylene and being caused by a $\pi_u \rightarrow \pi_g$ orbital change in the C=O link. These substances also have a characteristic absorption band in the longer ultra violet, about 2900A, of low extinction coefficient, but having no counterparts in the ethylenic molecules. The origin of this band lies in the oxygen atom. This has a shell of eight electrons; one pair in a orbital and one pair in a σ_g orbital are shared with the carbon in the C=O links. The other four are in the two remaining 2p orbitals of the oxygen, being in almost undisturbed atomic orbitals and taking little part in the chemical binding (two "lone pairs"). One of these orbitals will have its nodal

plane normal to the link, and the other's nodal plane will be along the link and at right angles to the nodal plane of the π_u bonding orbital. McMurray showed that the weak absorption characteristic of carbonyl compounds at 2900Å arises from an orbital change of one of the "non bonding" electrons passing from the p orbital, whose nodal plane is at right angles to that of the π_u orbital, to the excited π_g molecular orbital.

These orbitals are depicted in Fig. 2. The absorption at 3000Å is accompanied by the passage of one electron from the hour-glass shaped orbital d,d to the unoccupied anti-bonding orbital b.

Figure 2

ORBITALS OF THE CARBONYL GROUP C=O



Thick lines = σ_g type orbitals ("single links").

a = π_u orbital characterised by a nodal plane in the H.CHO plane. It contains two electrons in the ground state of the molecule.

b = π_g orbital characterised by one nodal plane in the molecular plane and another at right angles to the C-O link. No electrons occupy this orbital in the ground state.

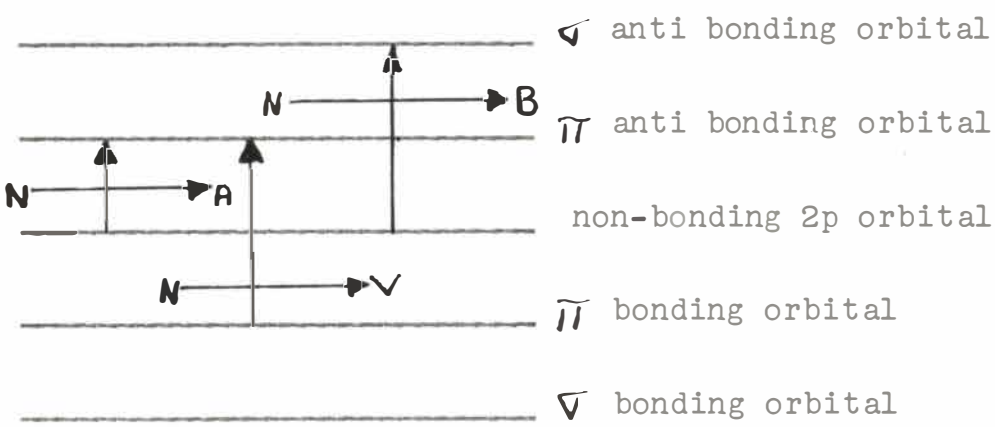
c,c and d,d = non-bonding p-type orbitals of the oxygen atom, each containing two electrons in the ground state ("lone pairs"), c,c has a nodal plane at right angles to the C-O link and d,d one in the plane of the paper.

Excitation of one electron from orbital a to b occurs on absorption of light at 1900Å while at 3000Å a transition occurs from d to b.

The three transitions which occur, are normally spoken of as N→A, N→V, and N→B, where N is the normal ground state, and A, V and B excited states. This is illustrated by Figure 3.

Figure 3

THE ALLOWED TRANSITIONS IN THE CARBONYL GROUP



The first ionization potential of carbonyl molecules is known (e.g.from Rydberg bands having very little vibrational structure) to correspond to the removal of one of the oxygen lone pair electrons. Consequently the sequence of decreasing binding energy for the electrons in a carbonyl group is

σ bonding electrons, π bonding electrons, non-bonding electrons

and the N→A transition is expected to cause the longest wave-length spectrum. The selection rules require this transition (in contrast to N→V and N→B) to be of low probability.

For simple carbonyl compounds such as aldehydes and ketones the longest-wave-length absorption takes the form of weak bands situated near 2900Å. The 2900Å systems are therefore interpreted as N→A in type. An example of this is the very weak absorption peak observed in fenchone at 2860Å (see APPENDIX I). If the carbonyl group is attached to a conjugated system the N→A transition will move to a longer wave-length because its upper state has been depressed. This can be seen in benzophenone where λ max is 3300Å (see Fig. 10). This effect can also take place in N→V transitions but not N→B.

Bond Polarity in Carbonyl Group.

Walsh (125) shows that an important factor effecting the

location of N⟶A, N⟶B, and N⟶V transitions is the magnitude of the polarity in the C=O bond. As the C=O bond polarity increases there will be increasing repulsion between the bonding and non-bonding oxygen electrons i,e, both the lone pair and bonding electrons will become more weakly bound. This means that all three transitions, N⟶A, N⟶B, and N⟶V move to longer wave-lengths.

A recent quantitative approach to the carbonyl group has been given by Hartmann (45) who has applied the Slater-Pauling treatment in solving a number of secular equations in order to obtain the energies of transitions.

Qualitative Discussion of Some Effects Found in Molecular Absorption Spectroscopy

1. Resonance.

With the advent of a paper published by Bury (16) in 1935, postulating the process of absorption of light in terms of the resonance theory, many books and articles have been written, both qualitative and quantitative, describing this phenomenon. Wheland (131) has given a good qualitative description; while Herzfeld has recently given a quantitative treatment (51).

The definition of resonance as given by Lewis and Calvin (65) is as follows. " A substance to which only one reasonable formula can be assigned has properties in accord with that formula. When to a substance two or more structures might be assigned, such that one may be derived from another merely by the shifting of electron pairs, these structures are said to be in resonance with one another, especially if the energies corresponding to the several structures, as well as the relative positions of the atoms, are not widely different".

Resonance will alter either the ground state or the first excited state and will have an overall effect of diminishing the energy difference between these two states, hence lowering the energy required for any particular electronic transition, and so shifting λ max to a longer wave-length. Care must be taken in making generalizations when dealing with resonance

energy and the absorption process, since the statement, "The greater the resonance energy the longer the wave-length of absorption", is sometimes far from true. An example of this is the isomeric molecules naphthalene and azulene; while naphthalene has a greater resonance energy than azulene, the former molecule absorbs at a much shorter wave-length than the latter (37).

In general, the colour of a molecule will be deeper the greater is the resonance among ionic forms or forms involving a separation of charges. Many authors have shown that λ max is larger for compounds exhibiting the greatest amount of resonance but in general, such resonance has involved the formation of polar structures. For instance, the values of λ max for aromatic amines are greater than those of the corresponding compounds without the amine group, owing to the resonance of ionic forms, as

while in acid solution such resonance is inhibited and the spectra revert to those of the parent aromatic compounds.

2. Steric Hindrance.

The effects of steric hindrance upon the colour of a substance are largely due to its interference with the resonance of the compound, either when the molecule is in the ground state of when it is in one of its excited states. Because of steric hindrance, the resonance may be limited to certain portions of the molecule and thereby effect its potential energy, and hence its λ max.

Several investigations have been carried out on the steric hindrance occurring in the excited state of organic molecules particularly the substituted biphenyls. The coplanarity of the rings is destroyed hence minimizing the conjugation and so the resonance. The overall effect is to shift the λ max to shorter wave-lengths corresponding to the monosubstituted benzenes.

Steric hindrance occuring in the ground state of the molecule will in general cause the molecule to absorb at longer wave-lengths than a similar compound in which the strain does not exist. This is due to an increase in the potential energy of the ground state, bringing about smaller differences in the energies of the ground and first excited states to allow a smaller excitation energy. The work of Brooker [14] et. al. on the cyanine dyes showed that there was no simple relationship between the area of overlap of the substituents and the shift of λ max to longer wave-lengths.

3. Effects of Substituents.

This effect will depend on three factors, (a) the type of substituent e.g. saturated or unsaturated, (b) the position of the substituent, (c) the type of molecule into which the substituent is introduced. The present work is concerned with alkyl sustitution in the para postion of a benzene ring.

The substitution of a hydrogen atom by a methyl group will lead to a repulsion of electrons, thus making them more mobile. This effect was termed by Ingold , "the inductive effect". The inductive effedt has been observed to increase in the series

methyl ethyl iso-propyl tert.-butyl

increasing + I effect →

where each methyl group adds to the repulsion of electrons. In general the result of such substitution on the spectrum is to produce a bathochromic shift. In recent years it has been noted that the order of magnitude of this bathochromic shift does not necessarily increase from methyl to tert.-butyl. Instead an effect called hyperconjugation is acting, displaying its greatest magnitude in the methyl group and zero in tert.-butyl. Induction and hyperconjugation can occur as conflicting effects. For a fuller treatment of hyperconjugation see page 74 .

In 1947 Price claimed [95] that "the sustitution of a hydrogen atom by an alkyl group always has the effect of lowering the ionization potential". Now the variation in ionization potential is proportional to the variation in λ max, i.e. lowering of ionization potential is equivalent to shifting λ max to a longer wave-length. However, in 1950 A. and B. Pullman [96] showed semi-quantitatively that hypsochromic shifts as well as bathochromic took place on alkyl substitution. Brown [15] has explained this very well, especially in connection with the first absorption band of a compound. He shows that substituents attached to a position of (local) low π electron density increase the frequency of the first absorption band, while in the position of high π electron density the frequency is decreased. This type of hypsochromic shift was observed with alkyl substituted azulene and alkoxy substitution in N-methylacridone. It is significant that substituents in alternant hydrocarbons, such as naphthalene, do not occasion these alternating effects, and it is just for these systems that the molecular orbital approximation indicates a uniform electron density around the ring system.

It is worthy of note that in the three examples given i.e. resonance, steric hindrance and substituent effects it is very difficult to guess the direction of the λ max shift unless considerable prior knowledge of the molecular structure is available.

Laws of Absorption.

Lambert's Law.

This law deals with the relationship between the thickness of a medium and its absorptive capacity.

I_o represents the incident energy;

I the transmitted energy;

l the thickness of the layer of the absorbing solution;

c the concentration of solute in the solution;

T_i the (internal) transmittance, or I/I_o .

Mathematical statements relating the quanities involved are found in two forms - logarithmic and exponential.

The logarithmic statement can be considered first. The absorption of energy (the decrease in intensity per unit thickness) is proportional to the intensity of the energy. Expressed mathematically,

$$-\frac{dI}{dl} = KI \qquad \text{(22)}$$

or

$$-\frac{dI}{I} = K\,dl \qquad \text{(23)}$$

Integrating between the limits I and I_o, and l and O, the following equation if obtained.

$$\int_{I_o}^{I} -\frac{dI}{I} = \int_{o}^{l} K\,dl \qquad \text{(24)}$$

$$-\left[\log_e I\right]_{I_o}^{I} = K\left[l\right]_o^{l} \qquad \text{(25)}$$

$$\therefore K = \frac{2{\cdot}303}{l}\left[\log_{10} I_o - \log_{10} I\right] = \frac{2{\cdot}303}{l}\log_{10}\frac{I_o}{I} \qquad \text{(26)}$$

The exponential expression states, that if a layer of unit thickness transmits a fraction t of the energy incident upon it, a thickness l will transmit the fraction t^l.

Then

$$I = I_o t^l \qquad \text{(27)}$$

This law may be expressed in the form,

$$T_i = e^{-\epsilon' l} \qquad \text{(28)}$$

where ϵ' varies with the wave-length of the incident radiant energy.

Beer's Law.

This second law expresses directly the relationship between the absorptive capacity and the concentration of the solution

$$T_i = t^c \qquad \text{(29)}$$

where T_i is the transmittance for a given thickness and t is the transmittance for a solution of the same thickness having unit concentration .

Combined Beer - Lambert Laws.

The two laws can be combined, and for a thickness the expression will be

$$T_i = t^{lc} \qquad \text{(30)}$$

The expression may be written,

$$T_i = e^{-\epsilon' lc} = 10^{-\kappa lc} \qquad \text{(31)}$$

and since $T_i = I/I_0$

$$I = I_0 e^{-\epsilon' \ell c} = I_0 10^{-K\ell c} \quad \text{(32)}$$

In the logarithmic form, more familiar to chemists, the expression for unit thickness can be written as

$$\log_e I/I_0 = \epsilon' c = \log_e T_i \quad \text{(33)}$$

$$\log_{10} I/I_0 = \epsilon' c = \log_{10} T_i \quad \text{(34)}$$

$$\log_{10} I/I_0 = \epsilon c = \log_{10} \frac{1}{T_i} \quad \text{(35)}$$

and for thickness ℓ

$$\log_{10} I_0/I = K\ell c = \log_{10} \frac{1}{T_i} \quad \text{(36)}$$

K is called the extinction coefficient;

ϵ is called the molecular extinction coefficient;

ϵ' is called the molar extinction coefficient.

These laws are only obeyed by dilute solutions within certain limits. Some of the causes for discrepancy are listed below:

(a) change in the refractive index with change in concentration;

(b) displacement of equilibrium involving the absorbing entities, such as ions;

(c) reciprocal interaction of the absorbing enitities, either among themselves or with solvent and foreign substances.

PART II

CHAPTER IV.

INTRODUCTION TO EXPERIMENTAL WORK.

Preparation of Diaryl Imines.

The compounds were prepared by the Grignard method which is a modification of that first used by Moureu and Mignonac [86] and more recently by Pickard and Vaughan [92]. This method appeared to be the easiest for the more complicated imines since the same apparatus and a similar technique coulb be used in all preparations.

The nitriles (benzonitrile and tolunitrile) were dried over anhydrous magnesium sulphate and then carefully distilled. All the reagents were carefully dried and then purified, where necessary by distillation or recrystallization.

It must be realised that the emphasis was not placed on obtaining a large yield although this was desirable, but on the purity of the product since for spectral work, this is imperative. Originally it was intended to make a study of the imines themselves. It was found however that the yields obtained (3 - 5 grams) were not completely free of impurities, there very probably being small amount of ketones (4 - 6%) which could not be separated by ordinary vacuum distillation, since the boiling points of the imines and corresponding ketones in the series were similar. The yields were too small for any more elaborate technique of separation, and as the major part of this yield had to be used for hydrolysis to ketone, (see below) care had to be taken not to destroy too much. This could be brought about by excess heating which may occur in distillation. In order to increase the yield, the quantity of starting material used would make the cost prohibitive. It was therefore decided that a solid should be used if possible since repeated recrystallization would only require small amounts, and a solid is usually easier to work with.

The imine hydrochloride appears to be a suitable compound to handle. This can be prepared with comparative ease by

bubbling dry hydrogen chloride through an ethereal solution of imine. The hydrochloride which is a salt, is insoluble in ether and so forms a precipitate. This can then be filtered and washed with ether to remove any organic impurities soluble in ether e.g. ketones. The salts are white and usually powdery, most of them subliming when heated. They can be readily recrystallized from chloroform, in which they are readily soluble, by addition of ether. The salts were washed repeatedly with ether. They were dried between filter papers, then in a vacuum oven at 70° and finally in a vacuum desiccator.

Due to the great instability of these compounds, the technique was developed for carrying out investigations in the following manner.

After the salt had been precipitated, it was dried in the oven for half an hour and vacuum desiccator for three hours. This was then analysed for nitrogen and chlorine. If an analysis lay within the limits of accuracy ($\pm$ 0.1 - 0.2% difference between the experimentally derived and theoretically calculated percentage of an element in the compound), the compound was immediately used for making the standard solution on which spectroscopic investigations were then carried out. This reduced to a minimum the possibility of hydrolysis since all precautions for dryness had been taken, and also the time factor between preparation and spectroscopic investigation of compounds, (about 6 - 7 hours).

The nitrogen content was analysed by the Kjeldahl method, the apparatus and technique being identical to that outlined by Belcher and Godbert (5).

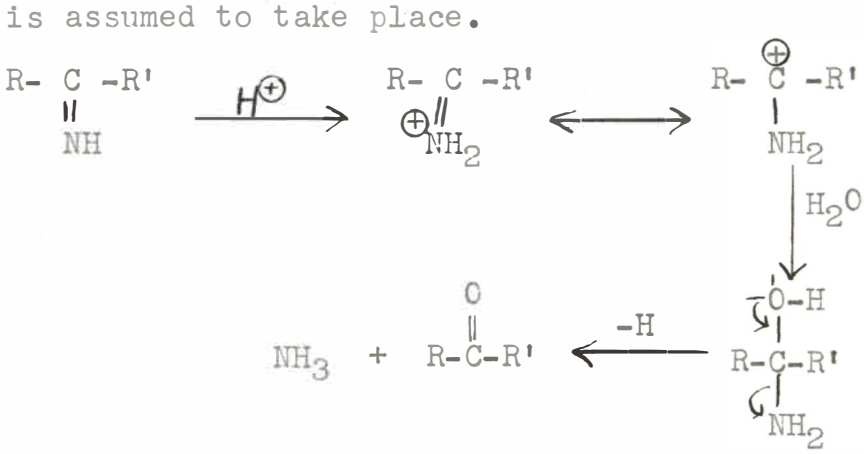
The chlorine content was analysed by the Robertson method. This consists of heating the salt with potassium dichromate and sulphuric acid, with the resultant formation of chromyl chloride which is absorbed in sodium peroxide. Excess silver nitrate is then added to precipitate silver chloride, the unused silver nitrate estimated by titration with ammonium thiocyanate. This is well outlined by Thorpe and Whiteley (117)

The Kjeldahl method gave the most reliable results, since

in the latter method the end point was more difficult to judge. However with practice the titration readings were found to be reproducible.

Diaryl Ketones.

Since the ketimines are related so closely to the ketones, it was decided to study a similar series of ketones, in order to observe whether any deviations occur in their absorption of ultra violet light. The hydrolysis of ketimines to ketones has been described by Moureu and Mignonac (86), Pickard and Vaughan (92), Shriner and Turner (105) and others. In many standard preparations of ketones, the ketimine is prepared as an intermediary without veing isolated. The reaction consists of boiling the imine with a dilute (IN), or in some cases concentrated ($\frac{5}{4}$N) acid, usually hydrochloric. The follwing is assumed to take place.



The ketones were distilled under reduced pressure and those that solidified at atmospheric temperature or above were recrystallized. The melting points were found and their oximes prepared by a method similar to that outlined by Vogel (120). These were then purified by recrystallization and their melting points found, which were then compared with those in the literature. This gave a double check of the purity and identity of the compounds. Tert.-butyl benzophenone appeared to be a new compound as no mention was found of it in chemical literature. This differed from the other ketones in the series since it was a pale yellow viscous oil which would not solidify even when placed in an ice-salt mixture. A complete analysis was carried out on it by Dr. A.D. Campbell of Otago University.

p-ethyl-, p-isopropyl- and p-tert.butyl- benzophenone were prepared by the hydrolysis of the imine. Benzophenone was taken

from stock and recrystallized a number of times from methanol until it reached constant melting point which agreed with the literature. p-methyl benzophenone was prepared by a Friedal-Crafts reaction [121].

Notes on Spectroscopic Investigations.

The spectroscopic observations were carried out between 2000 and 3500Å. One of the objects was to find whether any shift in absorption took place with para substitution. The emphasis was therefore placed on the relative absorption of these compounds (see page 72).

The compounds dealt with are too complex to apply any rigid mathematical treatment in order to elucidate the electronic structure. A semi-quantitative discussion will however be attempted in a later section, with the intention of comparing the results obtained in this work with those obtained by other workers. No quantitative treatment has been attempted for the imino group, since so very little experimental work has been attempted on them.

FIG. 4. THE HILGER UVISPEK PHOTOELECTRIC SPECTROPHOTOMETER

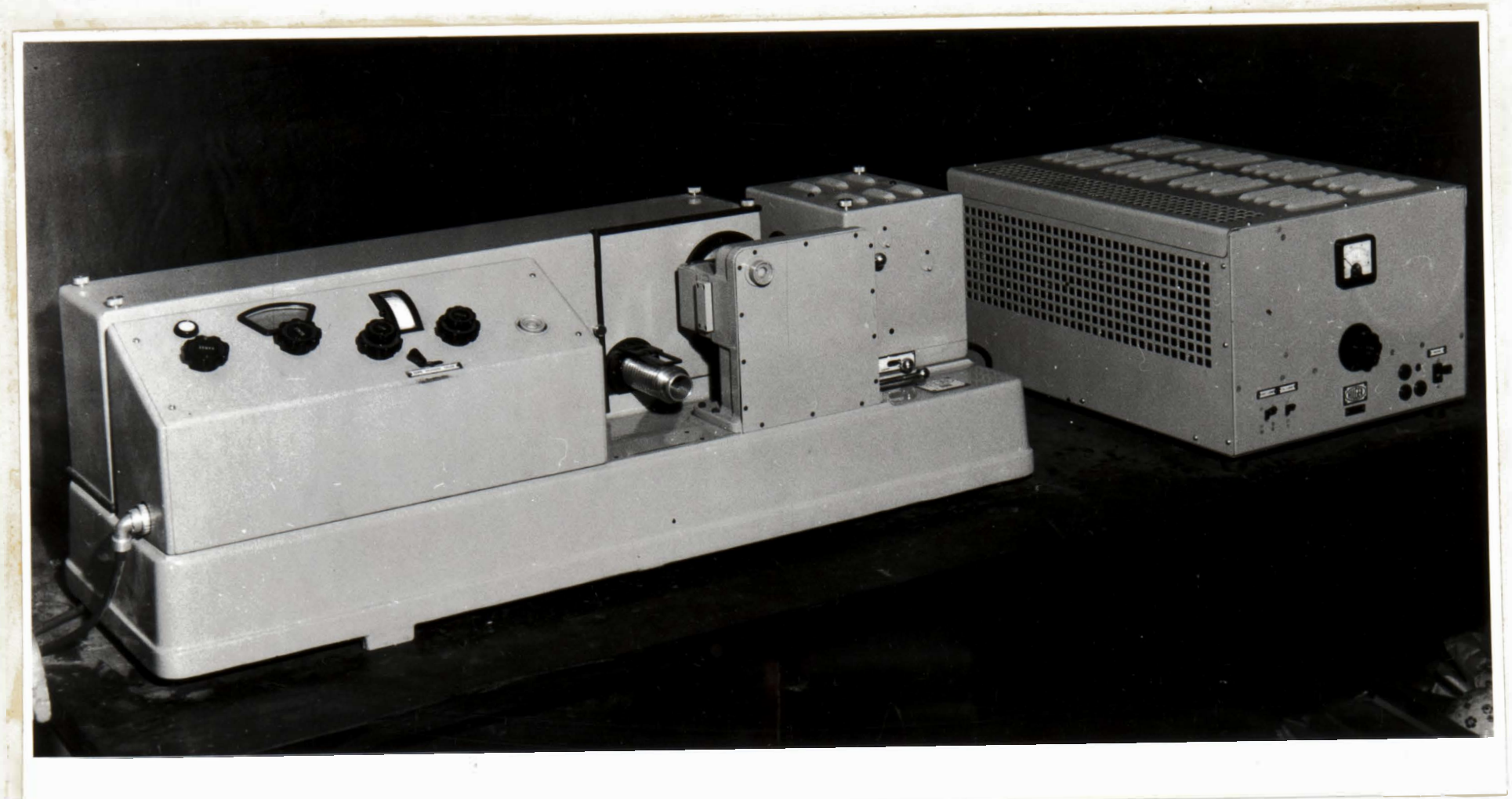
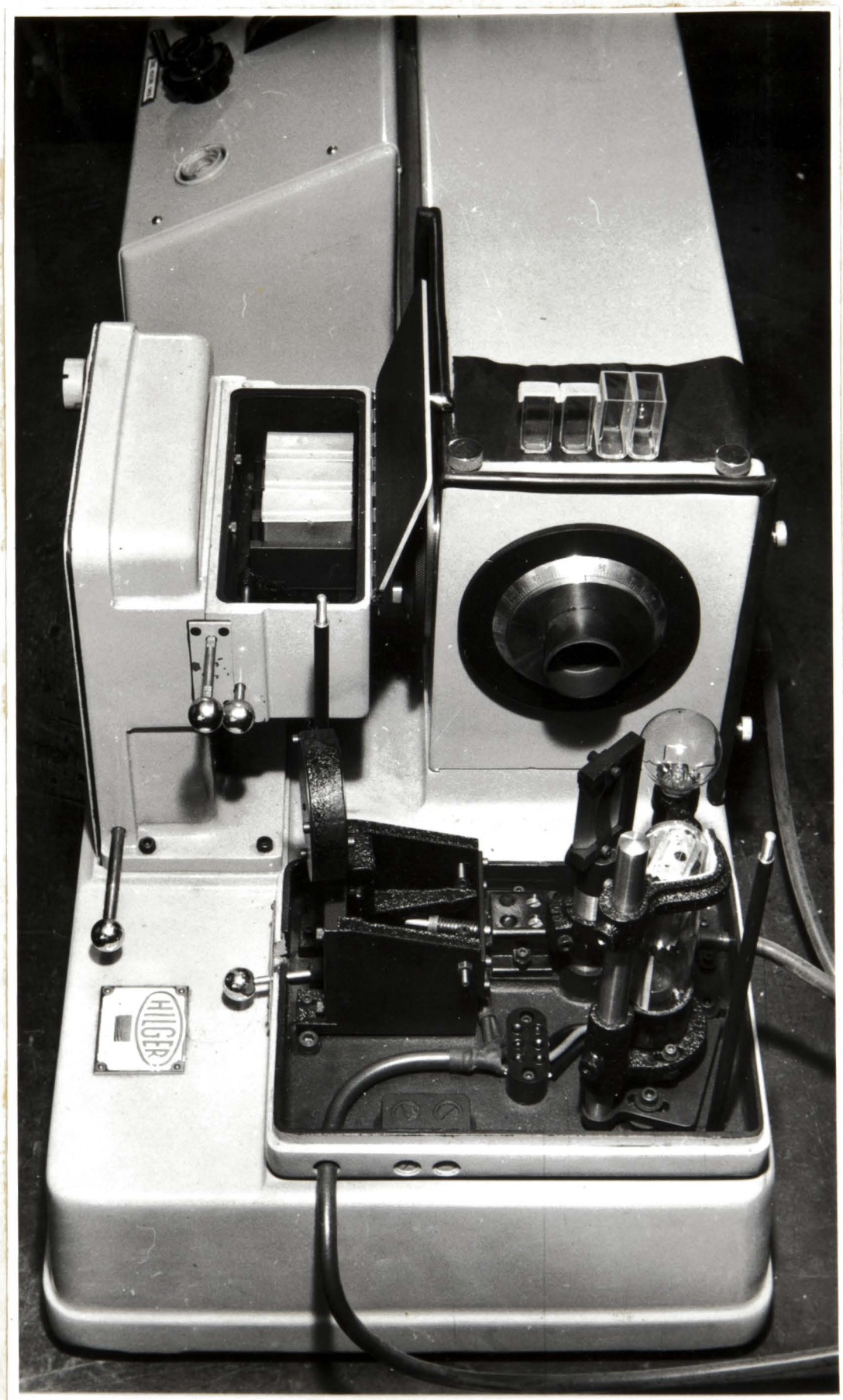


FIG. 5.

THE UVISPEK SHOWING LAMPHOUSE AND ABSORPTION CELLS.



CHAPTER V

DESCRIPTION OF SPECTROSCOPIC APPARATUS AND TECHNIQUE

General Description of Uvispek.

In obtaining one of the absorption curves for fenchone, the Hilger Medium Quartz spectrophotometer was used. This instrument has been described by Sheat [103] and Biggs [7] and no further mention will be made here.

All other absorption curves were obtained by using the Hilger Uvispek Photoelectric Spectrophotometer. This instument consists of two units only - the spectrophotometer itself, and a mains-operated power pack providing all the required supplies (see Figure 4). The spectrophotometer is built on an aluminium alloy base casting which carries the light sources, monochromator, absorption cells, photocells and the measuring unit.

(i) Light Sources.

To cover the whole spectral range of the apparatus two light sources are required, a hot cathode hydrogen dis charge lamp for the ultra violet, and a tungsten filament lamp for the visible, both mounted in a single ventilated housing. A movable mirror, operated by a small spring-loaded lever with clamping screw enables either type of lamp to be selected at will and without the need for individual adjustment.

The optical condensing system in the light source cabinet, produces an image of the light source on the entrance slit of the monochromator, so that the fullest possible use is made of the energy output from the sources. The stabilised supplies for operating these lamp sources are obtained from the power pack.

(ii) Monochromator.

This employs a Littrow dispensing system with a relative aperture of approximately f/10. The dispersing prisms (which may be of quartz or glass) are fitted into their own respective mounts which are inter-changeable and are fixed to the instrument.

Wave-length selection is obtained by rotating a drum attached to a micrometer screw, which turns the prism table. The drum carries a helical scale graduated in microns, and is

provided with a sliding index. The wave-length drum for the quartz prism is engraved to read from 0.2μ to 1μ .

(iii) Absorption Cells and Photocells.

These are contained in the photocell head. The appropriate photocell, in conjuction with an electrical measuring unit, measures the relative amount of light transmitted by the medium under test compared with the reference medium.

The absorption cells are accommodated in the enclosed chamber with lid adjoining the exit slit, and are carried in a three-compartment sliding tray moved by means of a notched rod so that any of the cells can be brought into the light path as desired. The cell chamber with cells are shown in Figure 5 .

(iv) Electronic Measuring Unit

A null method of measuring the photocell response is used, in which a counter E.M.F. is obtained from a calibrated potentiometer. Accurate setting is assured by the use of a D.C. amplifier and a null reading meter. The potentiometer scales are graduated in density (log I_o/I) and also in percentage transmission viz 100 (I/I_o) Three concentric scales cover the full range of densities from 0 - 3.2 in five overlapping ranges selected by means of a switch, which also controls the illumination of the selected scale.

Calibration of Uvispek.

The instrument was assembled by following the instructions given in the booklet supplied with the Uvispek. The wave-length drum setting was found inaccurate and was therefore reset. This was done by using an aqueous solution of potassium nitrate as a standard; data for this particular solution has been obtained by many workers [127].

By knowing the concentration of the solution and using the extinction coefficients given in the literature, the density for any particular wave-length was calculated (this follows from the Beer-Lambert rule where $\epsilon = \frac{d}{\ell c}$; ϵ, ℓ and c are known and d calculated). The potentiometer was then adjusted so that the density reading was fixed, and the wave-length drum

rotated by releasing the retaining screw, which had the effect of rotating the drum but not the prism. This was done over a r range of wave-lengths between 2500Å and 3300Å. The screw was then tightened, thus securing the drum in a fixed position. The method is essentially "trial and error", but the final curve obtained for the potassium nitrate solution was almost identical with that obtained by other workers.

Comments on Apparatus.

Only minor points of improvement of the apparatus can be suggested in this description.

(i) The Thermal Relay Switch.

This is incorporated in the power unit to limit the initial current through the lamp when first switched on, until the main control current is functioning properly. About two minutes is normally required for this warming-up period. It was found, however, that during readings, the electronic measuring device would tend to shift considerably from the zero setting. Investigation showed that the reason for this was the fluctuations which occurred in the voltage output of the mains. This resulted in periodic lowering of energy through the thermal relay, which, on reaching a certain minimum (215 volts), tended to switch off altogether. This relay was found to be of bimetallic type. The effect of fluctuation was thus corrected by placing a Variac with a constant output of 240 volts between the mains and power supply unit.

(ii) Absorption Cells.

It was found that although these cells were easy to handle and manipulate as well as being easy to clean, they were not entirely satisfactory for the type of work carried out, and in fact, their use was somewhat restricted.

1. As can be seen from Figure 5 , the cells have a U shaped cross section. They are in five sizes 0.1cm, 0.5cm, 1.0cm, 2.0cms., and 4.0cms. in length, each being covered by a polythene cap according to size. The cap covers the sides completely but not the ends; this results in evaporation.

With aqueous solutions the evaporation was not large, but with m more volatile solvents it was appreciable. With ether, using the 2cms. cell it was found that about 50% evaporation had taken place in ten minutes, and that it was impossible to repeat with any degree of accuracy two consecutive readings. Hexane is another solvent with a high vapour pressure although not as high as ether. It was found that this solvent could be used if the solution was changed every three or four readings. The solvent in which the major part of this work was carried out is methanol. With the larger cell evaporation was fairly small and about ten or twelve readings could be taken without changing the solution. With the smaller cells however, evaporation played an important role; about 20% of the solution evaporating in fifteen minutes. In this case a fresh solution was used every five readings.

2. Although of no importance in this particular work, another drqwback is the fact that the length of the cell is fixed. In some experiments where it is necessary or desirable to use a fixed concentration, while working at certain densities, this type of cell cannot be used.

Technique of Optical Work.

(i) Solutions.

The concentration of the solutions were in the vicinity of 10^{-4} moles/litre. The required compound was weighed by difference into the standard flask and the solvent then added. In order to obtain high accuracy in the weighing, a solution of 10^{-2} - 10^{-3} moles/litre was first made in a 50ml or 100 ml flask and then diluted to the required concentration.

(ii) Method of Taking Readings.

Prior to use, the cells were thoroughly cleaned by rinsing in distilled water and then drying. In taking readings over a range of wave-lengths, a trial "run" was always made to ascertain approximately where the maxima or minima lay. In these regions, readings were taken at intervals of 1m.μ. whereas in places where the slope of the curve was vertical readings were taken at intervals of 5m.μ. In the region

where maximum absorption took place, all the readings were repeated by using a new solution in the cells. In this way, experimental errors due to evaporation were avoided.

Purification of Solvents.

(i) Methanol.

Commercial methanol was purified in the manner described by Weissberger and Proskauer [128], this being the method most used in this laboratory.

Two litres of methanol was left standing over 50 grams of silver nitrate for upwards of a month. This was then refluxed for a period of six to eight hour s, and distilled. Only when the distillate gave no test for aldehydes and ketones was it collected. The former was tested with Fehling's solution, and the latter with a soltuion of 6N sodium hydroxide saturated with mercuric cyanide. Final drying was by refluxing over magnesium activated with iodine for thirty minutes with subsequent distillation. Only the middle fraction boiling at 64.4°C was collected for use.

This solution was tested spectroscopically with a reference cell containing distilled water and a maximum absorption was found to take place at 220mμ. On the Hilger Medium Quartz Spectrograph the methanol was shown to absorb very strongly between 200 - 220 mμ.

(ii) n-Hexane

The actual method used was an adaption of some of those mentioned by Weissbergerand Proskauer [128], in particular those described by Castille and Henri [19], and Ley and Hunecke [66].

About 100cc of fuming sulphuric acid was slowly added to two litres of commercial n-hexane (B.P. 65 - 70°). The colour of the acid immediately changed to a very dark brown. This mixture was then left shaking, in a 2½ litre Winchester bottle on a mechanical shaker for twentyfour hours. The hexane was then separated from the acid, 100cc of fuming sulphuric acid was again slowly added to the hexane, and the mixture shaken for a further twentyfour hours. This process was repeated five

times; each time the colour of the acid became less intense. The actual addition of acid to hexane was made in Pyrex flasks, since a large amount of heat was evolved. When the mixture had cooled sufficiently, it was transferred to a Winchester bottle. It was then shaken for twentyfour hours with a 10% solution of sodium hydroxide, the hexane decanted, and finally shaken for three days with potassium permanganate made alkaline with 5% sodium hydroxide. This was then washed three times with distilled water, and finally distilled in a 30 inch column packed with glass beads. The middle fraction boiling at 67 - 68° was collected.

A spectroscopic test with a reference cell containing distilled water showed that the maximum of absorption lies in the region below 200 mμ, indicating that the aromatic hydrocarbons had been removed.

Range and Accuracy of Spectroscopic Measurements.

A series of investigations were conducted to determine the limits of accuracy of the spectroscopic measurements. It was found that this depends on a number of factors which are outlined below.

(a) Size of the absorption cell used.
(b) Wave-length at which maximum absorption takes place.
(c) Concentration of the solution used.
(d) The solvent used.
(e) The densities at which readings were determined.
(f) Incorrect matching of absorption cells.
(g) Uncertainty of measurement of radiations.
(h) Slit width and stray light.
(i) Inaccuracy in the setting of the wave-length drum.

The discussion which follows will be restricted to the near ultra violet region i.e. 2000 - 4000Å, since all the measurements in this work were carried out in this range. The hydrogen discharge lamp was used as the source of light and the H660 photocell having a range from 200 - 6500Å was used to detect the transmitted rays. In a recent article on accuracy in infra-red intensity measurements, Martin (73)

outlined a series of errors which may exist, Many of these are equally applicable to ultra violet measurements and some will be outlined here.

(i) Uncertainty of Measurement of I_o and I

This can either be caused by variation in the source of radiation or in the sensitivity of the measuring system, whether electronic or galvanometer with photoelectric amplifier. This, expressed as a percentage of the radiation (I_o or I) being measured, can be regarded as independent of the quantity of radiation and can be represented as $\pm 0.01 I_o$ or $\pm 0.01 I$

From the Beer-Lambert law

$$d = \log_{10} I_o - \log_{10} I \quad - - - - - - - - - (1)$$

$$= 0.4343 (\log_e I_o - \log_e I) \quad - - - - - - - (2)$$

Considering firstly a variation of δI_o in δI_o, we have

$$\delta d = 0.4343 (\delta I_o / I_o) \quad - - - - - - - - (3)$$

so that

$$\frac{\delta d}{d} = \frac{0.4343 \delta I_o / I_o}{\log_{10} I_o - \log_{10} I} \quad - - - - - - - - (4)$$

Thus if $\delta I_o / I_o$ is 1%, the corresponding percentage change in for $\delta I / I = -1\%$. The values of $\delta d / d$ are only strictly correct when $\delta I / I$ or $\delta I_o / I$ is small, (1%), although it can in some cases become quite large e.g. when the densities are large.

In the present work a Variac was used to steady the input into the electronic power unit. This power unit also steadied the output, hence it is doubtful whether the error would be as large as $\pm$ 1%.

(ii) Setting of Wave-length Drum

The accuracy of setting the wave-length drum was within a fraction of an Ångstrom unit between 2000 - 2200Å; between 2200 - 2500Å. it was from one to two Å; between 2500 - 3000Å. it was from two to four Å; while from 3000 - 4000Å the error would be in the order of four Å to one $m\mu$. Hence in the region 2000 - 3000Å. where most of the work was carried out, it is doubtful whether the error due to incorrect drum setting would exceed $\pm$ 0.5%.

(iii) Incorrect Matching of Absorption Cells.

The cells were checked when filled with distilled water and also when empty to find whether there was any serious disagreement

in their construction. The results showed that all the cells (with the exception of the 0.1cm, which was not used for the diaryl series) agreed to within a density of 0.005. The cells, being part of the optical system, were handled with the utmost care. The surfaces were not touched by the hand or any other greasy surfaces. Each time a solution was changed during a "run", the surfaces were carefully wiped with lens cloth to remove any dirt or dust. It was then replaced and the last reading repeated, this having the dual purpose of finding whether the cell was in position, and if any change in concentration had occurred due to evaporation. Errors due to changes in cell orientation and surface dirt may be encountered whenever cells are handled, cleaned or in any way moved from the cell carrier. To minimise any errors the cell constants were checked before and at the finish of the work, by taking the density reading at a wave length where the solution used had no absorption . If the density value was within 0.005, then the readings were accepted.

Caster [18], in commenting on this type of error as found in the Beckmann Spectrometer, has derived statistically from a number of results that the error should not be greater than 0.55 % for carefully matched quartz cells. With microcells it is possible to introduce an error as great as 20 - 50% due to incorrect centering of the cells. Twyman and Lothian [119] show quantitatively how incorrect orientation of cells can lead to errors. Suppose that the normal cell makes a small angle i with the incident light beam. If n is the refractive index of the absorbing medium, it is seen that the fractional error δ in the path is given by

$$i = n\sqrt{(2\delta)} \qquad (5)$$

For instance if $n = 1.3$ and $\delta = 0.0015$ then $i = 4^{o}6'$. Thus the cell should be set with its plane surfaces perpendicular to the light ray to within 4^{o}.

(iv) Errors Due to Stray Light and Slit Width.

Zscheile [133], in describing the construction of a photoelectric spectrophotometer using a Hilger Monochromator,

records a series of experiments carried out to test the effect of scattered light. He found that by keeping the concentration constant and varying the cell length from 1cm to 10cms., the effective scattered radiant energy at 232 mμ using the hydrogen arc was 0.1%. The slits were 0.90 mm wide.

Caster [18] stresses the importance of change in slit widths in the Beckmann quartz spectrophotometer while Zscheile [133] gives a comparison of results on absorption by chlorophyll a and b in the region between 4000 and 6600Å. The Hilger monochromator which the latter used gave densities which were somewhat higher than those obtained by the Beckmann instrument.

In the Uvispek the slit w idth used varied from 2.0mm at 210mμ to 0.14mm at 700 mμ. No noticeable change in density appeared at any time when the slit width was changed. The slits were usually adjusted at the points where the slope of the curve was vertical i.e. where absorption was neither a maximum nor a minimum, so that any very slight change in density which might occur would not be critical.

(v) Probable Error in a Measurement of the Optical Density.

It has long been recognised that it is bad practice to make measurements when the transmission is close to 0% on the one hand, i.e. above a density of 3.0 or to 100% on the other i.e. a density close to 0.0. In the first case a small amount of stray light will lead to a large error in the optical density, while in the latter, a small error in the measured transmission of blank or sample will lead to a serious error in density. On general grounds, it is to be expected that the most favourable region for accurate measurement is around 50% transmission and most authorities accept this figure.

Twyman and Lothian [119] state that the condition for accuracy in absorption-measurements is that the percentage accuracy in the measurament of an extinction coefficient is a maximum, thus implying a minimum value for $\frac{Sd}{d}$.

FIG. 7.

POTASSIUM NITRATE IN AQUEOUS SOLUTION

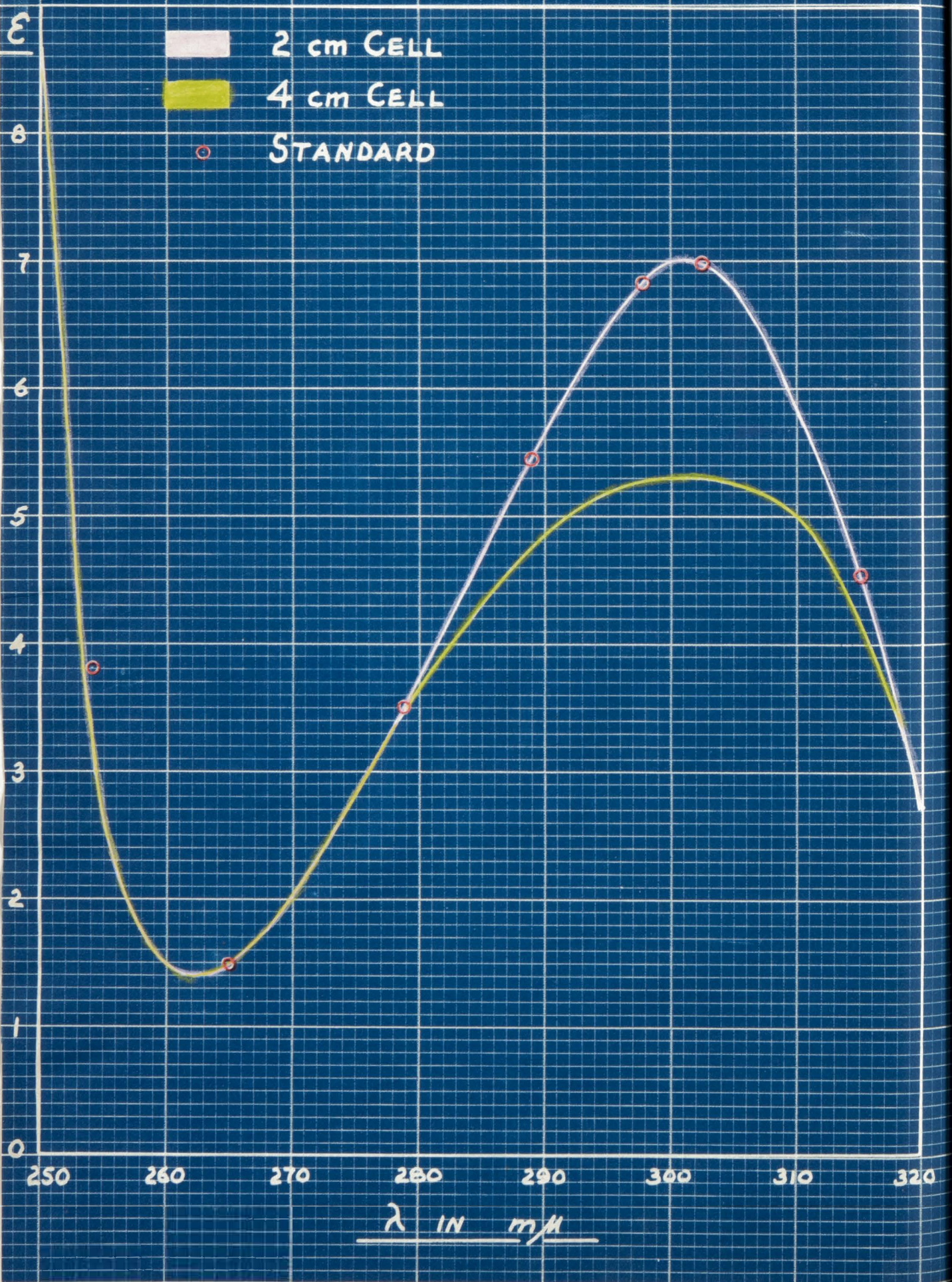
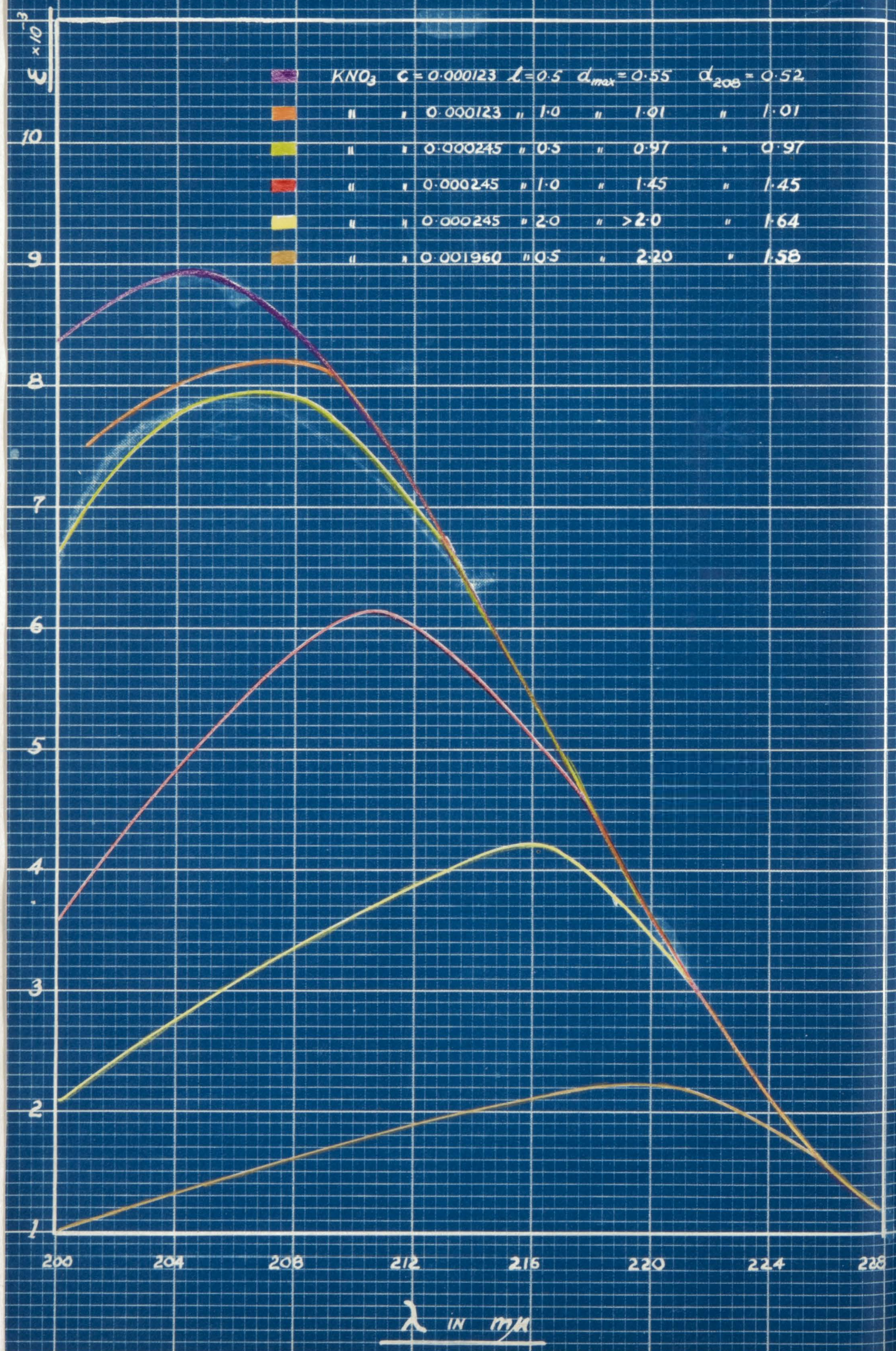


Fig. 7a.

Potassium Nitrate in Aqueous Solution



Now from equation (1) on page 51

$$d = \log_{10} I_0/I$$

on differentiating $$\delta d = -\log_{10} e \, \delta I/I \qquad (6)$$

$$\therefore \frac{\delta d}{d} = -\frac{\log_{10} e}{I d} \cdot \delta I \qquad (7)$$

$$= -\frac{\log_{10} e}{I_0 d 10^{-d}} \cdot \delta I \qquad (8)$$

To find the optimum value of d, the condition must be found when expression (8) has a minimum value i.e., when $d10^{-d}$ from (8) has a maximum value.

Thus, differentiating and equating to zero, the result obtained is

$$\frac{\partial (d 10^{-d})}{\partial (d)} = 0 \qquad (9)$$

$$\frac{\partial}{\partial (d)} (\log_e d - d \log_e 10) = 0 \qquad (10)$$

$$\frac{1}{d} - \log_e 10 = 0 \qquad (11)$$

$$\therefore d = \frac{1}{\log_e 10} \qquad (12)$$

$$= 0.4343$$

this being the best density to use. In order to see how critical this is, a series of values for d can be taken and the change in $d\,10^{-d}$ observed from equation (8).

d	1	0.8	0.43	0.2	0.1
$d10^{-d}$	0.100	0.127	0.159	0.126	0.079

This shows that densities 0.2 to 0.8 can be used without any considerable loss in accuracy.

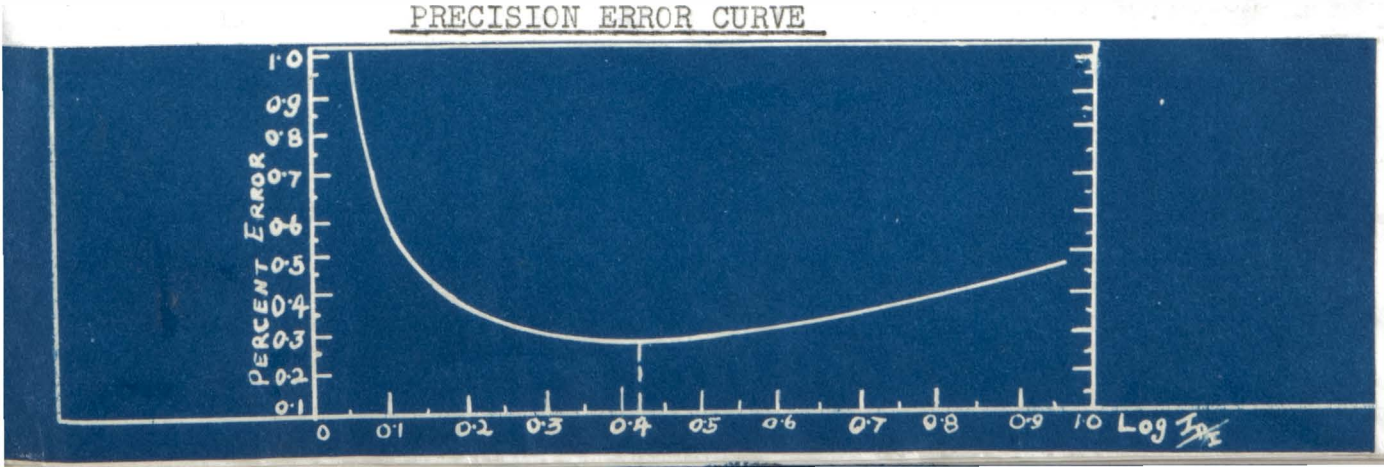
Zscheile (133) has calculated a number of points at different densities by using equations (1), (2), and (3), giving a plot of

$$\log I_0/I \quad \text{Vs.} \quad \frac{\frac{\delta I}{I_0} \times \frac{I_0}{I}}{2.3 \log \frac{I_0}{I}}$$

In this way he calculated per cent error with respect to density.

Figure 6

PRECISION ERROR CURVE



On the Uvispek used in this work, the density at which the majority of readings were taken was between 0.25 and 1.0. In some cases where the readings exceeded 1.2 they were repeated by diluting the solution and working in the lower and more accurate range. It was found that any density above 1.5 was not accurate, and the extinction coefficient of the peak began to drop, while the general outline of the curve became broader. The curve of potassium nitrate, obtained by Panckhurst[90], having a λ max at 300 m.μ shows this effect very well, see Figure 7. The fenchone oxime curve (Figure 8) shows this effect also, but other causes enter here as well (see below).

One of the reasons for this discrepancy, viz. stray light, has already been stated; another is very probably the insensitivity of the photocell. At a very high density i.e. when very little light is transmitted, the cell appears to give a current which is representative of a greater amount of energy than is actually falling on it. This will lead to a greater value of $\log. I_o/I$ i.e. d .

(vi) Errors in Non Linearity of the Measuring Unit.

Owing to the low intensity of the hydrogen arc lamp, and the relatively low insensitivity of the photocell at wave-lengths near 200 m.μ, certain effects occur which otherwise are not noticed at higher wave-lengths except at high densities. These may be caused by any one of the following, or the summation of all of them;

(1) Large absorption cells;

(2) High concentration of solution;

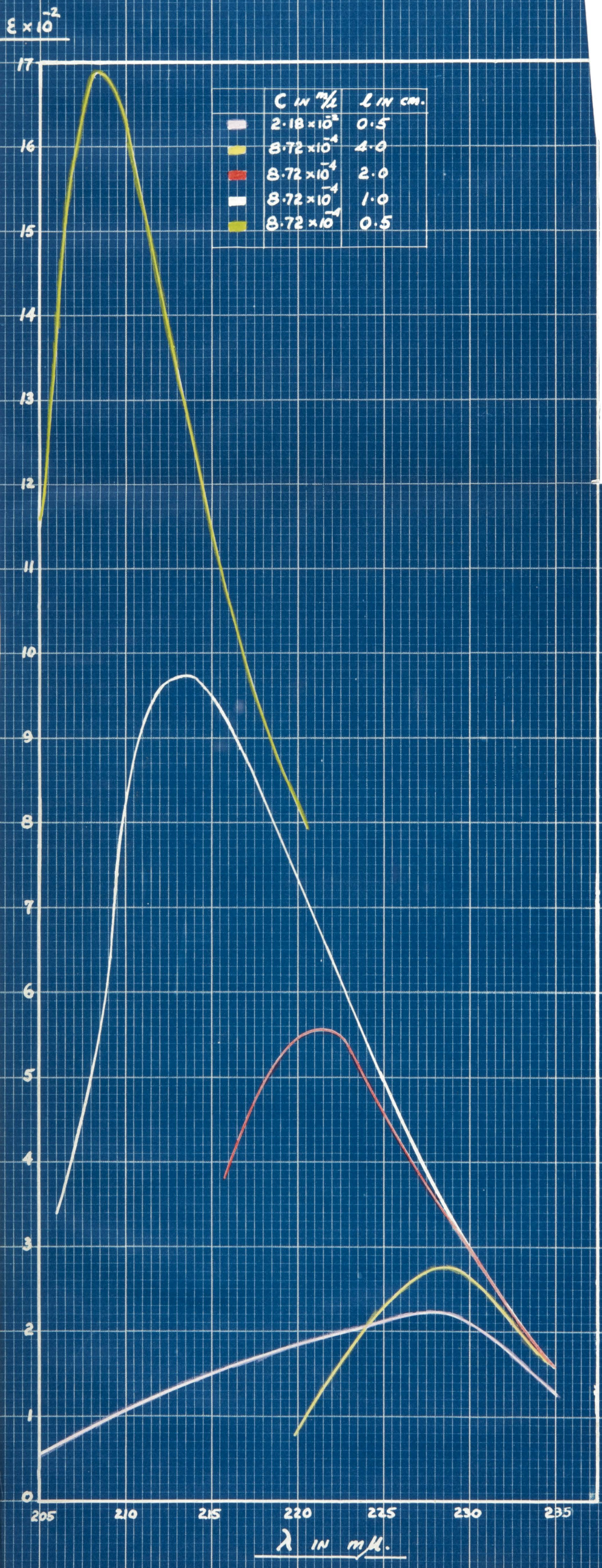
(3) A solvent which ab sorbs in this region;

(4) High densities.

The overall result of these complications is to lower the extinction coefficient and to move the apparent absorption towards a longer wave-length. In many cases, a peak of maximum absorption is obtained which is not representative of the compound. Examples of this are the peaks obtained for potassium nitrate. Under different conditions of concentration and density absorption peaks were obtained varying from 204 - 220 m.μ although in actual fact the solution absorbs

FIG. 8.

FENCHONE OXIME IN METHANOL

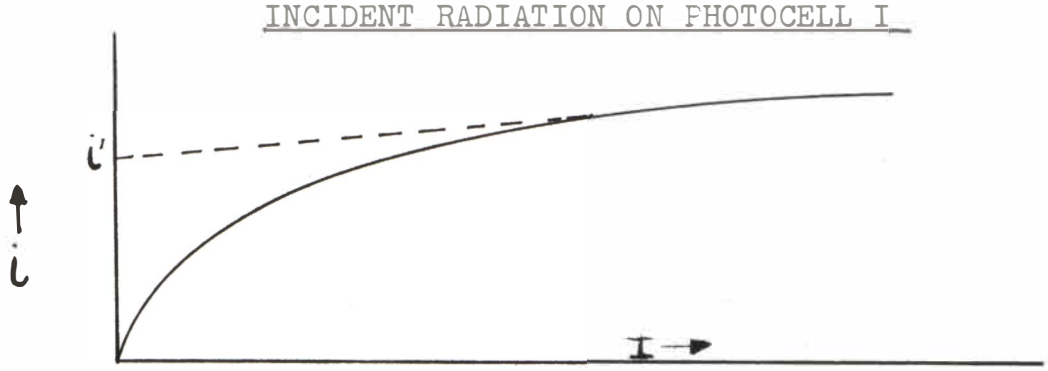


at 200 (see Figure 7a). Another example of this, is the fenchone oxime curve (Figure 8) for which no data could be found in the chemical literature. The group of curves obtained at different concentrations, cell lengths, and density show a remarkable series. The bottom curves have low extinction coefficients and are very flat. The top curve is pointed, and lies at a lower wave-length and higher extinction coefficient. If the solution were to give a series of constant absorption peaks, by using different concentrations and cells, then it would be correct to assume the reliability of the data. In this case the peaks can only be taken as imaginary, although it may be assumed that the sharp one is close to where the real peak is situated.

These results may have more than one cause e.g. fluorescence (see below), stray light, as well as non-linearity of the measuring system. However, it appears that the latter plays the greatest role in the regions below 220mμ, and at very high densities. This is illustrated in Figure 9.

Figure 9

A PLOT OF PHOTOCELL CURRENT OUTPUT i VS. INTENSITY OF INCIDENT RADIATION ON PHOTOCELL I



The phenomenon occurs when the intensity of light falling on the photocell is small. It can be seen from Figure 9. that only a very small change in the intensity will create a larger change in the cell current. The electronic measuring device does not compensate for this non-linearity and so the discrepancy results. This occurs at a higher wave-length, when the density is comparatively high (above 1.5); s showing that at a certain intensity the linearity is destroyed. The probability that Figure 9. represents this effect can be seen in the fenchone oxime curves (1, 2, 3, and 4); a maximum density of 0.9 was reached for each curve although the

the concentration was varied. Also in the potassium nitrate curve Figure 8., a maximum density was reached, hence resulting in a flat "peak". This is one of the arguments which can be given for non-linearity, and against fluorescence. If fluorescence occured, it would probably be noticed at lower densities as well, even if only to a slight extent.

Solvents absorbing strongly in the region of 220 mμ, and below enhance this effect. It is not noticed with pure solvents which absorb in the far ultra violet e.g. water.

(vii). Errors Caused by Fluorescence.

The large magnitude of errors, which can be caused by fluorescence is well outlined by Braude and co-workers (12). In photocell spectrophotometers the errors are much larger than in the photographic type, since the radiations under the measuring unit immediately after passing through the absorption cell. The importance which fluorescence plays is proportional to the size of the cell, the concentration of the solution, and the density. The larger these factors, the more pronounced are the discrepancies in the extinction coefficients. This is to be expected since when the cell is longer, or the solution more concentrated, the re exist more molecules in solution which will fluoresce. Similarly at very high densities i.e. above 2.0 where the transmitted radiations are 1/100th of the incident radiations, it is possible that the intensity of fluorescent radiations will be higher than the transmitted ones, and hence an overall effect of lowering the density, and thus the extinction coefficient will result.

In the compounds studied in this work, it is very doubtful whether any marked fluorescence occurred. Apart from the fact that no fluorescence was detected visually, the extinction coefficients obtained over a range of densities from 0.25 - 1.5 for either different concentrations or cell length were within 1 or 2% of each other. Braude (loc. cit.) giving examples of fluorescence, shows that the error is often as great as 30% in this range. One example of this is naphthalene in ethanol, λ max = 2200Å

10^4C	0.012	0.065	0.15	0.25	0.35	1.55
l	———	———	1.0	———	———	
d	0.119	0.618	1.39	2.05	2.35	2.32
e	99,000	95,000	93,000	82,000	67,000	15,000

10^4C	———	0.47	———	
l	0.1	0.2	0.33	0.50
d	0.518	1.16	1.69	2.28
e	110,000	108,000	108,000	97,000

The construction of the cell holder in the Uvispek is such that the absorption cells during a measurement lie with one face close to the exit slit, and the other towards the photocell. Now the distance between this first face and the exit slit is fixed while the distance between the second face and the photocell depends on the length of the absorption cell; the shorter the cell the larger is the distance. Fluorescent radiations are dispersed in all directions, hence the greater the distance between the dispersion medium and the measuring unit, the smaller is the amount of fluorescent radiations falling on the photocell. This is due to the geometric arrangement only. From the above considerations it follows that the small cells should be used whenever possible.

(viii) Accuracy of Spectroscopic Measurements.

1. In obtaining λ max for the absorption peaks the error lay within $\pm$ 5 Ångstrom units.
2. The extinction coefficients may show an error as high as 5%, but it may safely be taken that the error does not exceed 2 - 3%.
3. High accuracy can be obtained in measuring densities betw een 0.25 andl.0, while in some cases densities as high as 1.5 are reliable; however, densities above these cannot be accepted as accurate. It is also desirable to keep the cell size as small as possible.
4. With solvents which do not absorb above 2000Å (water and hexane), and using dilute solutions, small cells, and low densities, it is safe to assume that all readings above 2100Å are correct. With solutions having solvents which

do absorb in the near ultra violet i.e. ethanol and methanol, readings above 2200Å can be accepted as correct. All readings below these limits must be reviewed with care and on their own merits.

5. Comparison of results obtained with this instrument, and those obtained with others, may often vary considerably. This does not always show inaccuracy of measurement, since certain types of instruments [133] have been known to give highly reproducible results, yet when compared with others of similar manufacture have been found to vary as much as 6%, as in the case of the Beckmann Spectrophotometer [36].

CHAPTER VI

PREPARATION OF COMPOUNDS

The Diaryl Series.

Description of Apparatus.

The apparatus used in the preparative work for ketimines and that used in their hydrolysis to ketones, consisted of a four necked, "Quickfit", 300cc flask. The central neck held a mercury-sealed stirrer which was run at a constant speed of about 500 r.p.m. The three remaining necks (size B14), each held a double surface condenser (Davies type), a dropping funnel and a thermometer well, respectively. The latter were of two sizes; one that could extend to two or three cms from the bottom of the flask and used in measuring the temperature of the solvent during Grignard preparations. The other was shorter and level with the height of the condenser when used for distillation. The condenser was made to perform the double duty of refluxing and distillation. When required for the latter purpose, it was taken out of its normal vertical position and a semi-circular piece of tubing with a B14 cone at each end introduced into the neck, while at the other end of this adapter was placed the upper end of the condenser having a B14 socket. In this manner very little time was wasted in setting up the condenser and the same apparatus was used. The dropping funnel could also be replaced by a bubbling tube having a B14 cone. This was used when ammonia was bubbled through the system.

The apparatus was very satisfactory, since it left very little opportunity for leakage of gases and vapours, which corks would permit. Rubber bungs were unsatisfactory since organic solvents tended to react with the rubber.

Hydrogen Chloride Generator.

The apparatus was that described by Libman [68]. It consists of concentrated sulphuric and hydrochloric acid in the

ratio of 4:1 dropping onto a central column surrounded by a spiral tube on which they react. The hydrogen chloride gas, thus formed, passes through a wash bottle containing concentrated sulphuric acid and is then tapped off. The waste acids are forced up another column by the pressure of the gas and are expelled in a continuous process.

Chemicals:-

The halides and nitriles used in the preparation of the Grignard reagent and finally the ketimines were purified, firstly by drying over calcium chloride, as for benzonitrile, or anhydrous magnesium sulphate for the halides, and then distilled. The solvents such as ether and toluene were purified by, firstly, distillation and then dried by standing over sodium wire. The magnesium used in the Grignard formation was the commercial material produced for this purpose.

All care was taken in keeping the chemicals as dry as possible, since most of the preparations were carried out with small quantities and any moisture would have an adverse effect.

Preparation of Benzophenone Imine.

In the following preparations the Grignard reagent was prepared by a method described by Gilman et. al. (41); this reagent was then used to react with the nitrile in a manner described by Pickard and Vaughan (92).

Prior to use, all the apparatus was dried in an air oven at 110°. 0.15 gram atoms (3.6g) of magnesium were placed in the flask which was then attached to the apparatus consisting of:- the stirrer, the condenser with calcium chloride drying tube at its upper end, the dropping funnel, and the long thermometer well previously described. After the apparatus had cooled, 15cc of ether and a small crystal of iodine were added. 0.13 moles (20.0g) of purified bromobenzene were then placed in the dropping funnell and 20 drops added to the contents of the flask. This mixture was then refluxed gently for 10 minutes by heating the flask in a thermostatically controlled heating mantle.

At the end of this period, 55cc of ether was added to the bromobenzene in the dropping funnel which was then shaken to form a homogenous solution. The stirrer was then started. The ether halide mixture was then added at room temperature by regulating the dropping funnel to give a uniform flow - (about 20 drops per 10 seconds). Stirring was continued throu-out this addition period and also until there was no further evidence of reaction. (This was noted by stopping the stirrer and observing whether any bubbling occured at the surface). When no further reaction was taking place, the mixture was again heated (while still stirring) and refluxed for 20 minutes.

Half of the original volume of ether (35ml) was then distilled off (by using adaptor and condenser as described above) and replaced by an equal volume of dry toluene. The mixture was now further distilled until the temperature reached 100^{o}, and toluene of equal volume to the distillate added to the flask.

The condenser with drying tube was now replace in its normal position and the mixture gently refluxed. At this stage 0.1 mole (10.3 g) of purified benzonitrile was placed in the dropping funnel and slowly added over a period of 40 minutes with continuous stirring. It was noticed that the reaction was fairly violent in the addition, and the colour slowly changed from a brown to a cream. After two or three hours, the formation of a precipitate was noticed. Refluxing and stirring was continued for 48 hours after the addition period.

At the end of this time the calcium chloride tube on the condenser was replaced by a tube containing soda-lime and the dropping funnel replaced by the bubbler. A rapid stream of ammonia, dried by passing through two drying towers containing soda-lime, was then bubbled through the mixture at room temperature, while continuing to stir. The reaction was exothermic and solidification of the mixture in the flask took place within 10 - 15 minutes. At this stage 40cc of ether was added while stirring and bubbling were continued

for an hour longer. It was noticed that during this period the volume of solvent decreased.

The condenser, stirrer, bubbler and mercury well were then removed and 20cc of ether added to the flask. The necks were stoppered with corks and the flask shaken vigorously for 10 minutes. The contents were then centrifuged and the ethereal layer containing the dissolved ketimines separated. The solid was then placed back in the flask and the process repeated twice more. The ethereal solution was then dried for 2 - 3 hours over magnesium sulphate and the solvents (containing mainly ether and a little toluene) distilled off at atmospheric pressure. The ketimine was then distilled under reduced pressure produced by a water pump. After repeated distillation, 2 grams of a very pale yellow oil was obtained. B.P. 154° - 156° at 16mm, $n^{18^{\circ}}$ = 1.609. MW. (by depression of freezing point of benzene)=176 (Calc. for $C_{13}H_{11}N$ = 181).

Hydrochloride.

The ketimine was dissolved in 20ml of dry ether and placed in a 6" x 1" test tube with a side arm. Hydrogen chloride was then slowly bubbled through this solution until no further precipitation was noted. The product was a white solid salt being the ketimine hydrochloride. This was recrystallized three times from chloroform by the addition of ether, the precipitate filtered on a button filter at the pump and washed with ether. This was then dried in an oven at 50 - 60° for 15 - 20 minutes and then placed in a vacuum desiccator. The compound sublimed between 270 - 300° and melted at 310°. (Found: Cl, 16.20; N, 6.41. Calc. for $C_{13}H_{12}NCl$: Cl, 16.31; N, 6.45%).

Benzophenone.

The commercial substance was recrystallized twice from alcohol, giving a constant melting point each time = 48°.

p-Methyl Benzophenone Imine Hydrochloride.

The experiment was carried out in a manner identical with that of benzophenone imine to the point where the ethereal solution was obtained. In this case however, the imine was not

distilled but the hydrochloride formed directly, as was done in all the following cases. The quantities used were: bromobenzene 0.2 moles (30g), magnesium 0.23 moles (5.8g), toluene 0.054 moles (7g), ether 90cc. The nitrile being a solid, it was dissolved in 10cc of toluene. The product obtained was 3g of salt showing slight sublimation prior to melting at 244°. (Found: Cl,15.32; N, 5.96, Calc. for $C_{14}H_{14}NCl$: Cl, 15.32; N, 6.06%).

p-Methyl Benzophenone.

This was prepared by a Friedal-Crafts method analogous to that described by Vogel[120] for benzophenone.

Into a 250ml round bottomer flask was placed 60ml of dry A.R. toluene and 18g (15ml) of redistilled benzoyl chloride. To this were then fitted a condenser and stirrer which was started. Next 15g of anhydrous aluminium chloride was added during a period of 10 minutes. The flask was then placed into a thermostatically controlled heating mantle and the mixture refluxed for 3 hours. At the end of this period, the contents of the flask, while still hot, were poured into a mixture of 100g of crushed ice and 50ml of concentrated hydrochloric acid. The upper toluene layer was separated, filtered and washed firstly with 50ml of 5% sodium hydroxide solution and then with water. The toluene solution was then dried over magnesium sulphate and the toluene was evaporated. The ketone was then distilled at atmospheric pressure and came over at 311 - 312°. It was distilled twice from alcohol giving a constant melting point 57 - 58°.
Beilstein gives 59°. Yield was 12g.

Formation of p-Methyl Benzophenone Oxime.

Preparation similar to that described by Vogel [120] for benzophenoneoxime.

1g of ketone 0.75g of hydroxylamine hydrochloride, 4ml of alcohol and 1ml of water were placed in a 50ml round-bottomed flask. To this was added 1 gram of powdered sodium hydroxide in portions while shaking the flask. A reflux

condenser was then attached to the flask and the contents refluxed for 15 minutes. The flask was then cooled and the contents poured into a beaker containing 10ml of water and 2ml of hydrochloric acid. The precipitate formed was now filtered at the pump and recrystallized from methyl alcohol. It was then dried in an oven at 60° and in a vacuum desiccator. Melting point = 136.5° (Smith [108] gives 136 - 137°).

p-Ethyl Benzophenone Imine Hydrochloride.

Preparation of p-Bromo Ethyl Benzene.

The preparation was carried out in a fume cupboard. 0.75 moles (80g or 92ml) of ethyl benzene, which had been dried over calcium chloride and then distilled, was placed in the 300ml flask equipped with stirrer and dropping funnel. The flask was then covered with three layers of glazed black cloth and placed in an ice bath. 120 grams of bromine (B.P.) were then placed in the dropping funnel and slowly added over a period of one hour with continuous stirring. The stirring was continued for 4½ hours longer, the temperature being kept between 0 - 5° throughout.

The colour at this stage was a very deep red. The reaction mixture was now shaken with 4 lots of 50cc's of 10% sodium hydroxide solution and twice with water, the colour changing to a light yellow and eventually colourless. It was now left drying over magnesium sulphate for 12 hours and distilled. Obtained 30g of colourless liquid. B.P. 197 - 200°. $n^{17°} = 1.550$.

The physical constants of this compound as found by other workers [116, 27, 101, 60] appears contradictory. Thorpe [116] gives B.P. as 199° whereas Sapay, Varma and Subramonium [101] give it as 188 - 189° at atmospheric pressure. Oppernhaver, Roy and Marvel [27] give $n_D^{20°} = 1.5462$.

Preparation of the Ketimine.

This compound was prepared in a manner identical with that for benzophenone imine. The quantities used were:- 0.16 moles (30g) of p-bromo ethyl benzene, 0.2 moles (5.0g) of magnesium, 0.12 moles (12.5g) of benzonitrile and 85ml of ether. The

product obtained was 5g of a very light yellow oil B.P. 176 - 178° at 10mm and $n^{22°}$ = 1.5962. (Found: N, 6.30. Calc. for $C_{15}H_{15}N$: N, 6.69%).

It was not possible to get the sample more pure even after repeated distillation.

The Hydrochloride.

This was prepared as in the case of benzophenone. Obtained: a white salt M.P. 264°. (Found; Cl, 14.30; N, 5.58 Calc. for $C_{15}H_{16}NCl$: Cl, 14.45; N, 5.71%).

Formation of p-Ethyl Benzophenone.

4 grams of crude imine were placed in 100ml flask and 20ml of 6N hydrochloric acid added. This was then refluxed for 40 hours. The ketone was extracted with ether and the ethereal solution washed with water. This was then kept standing overnight with magnesium sulphate to dry. The ether was then evaporated and the ketone distilled a number of times in a 5ml flask with a 3" refluxing column. The fraction B.P. 318 - 320° was collected; $n^{22°}$ = 1.5917.

Oxime.

The oxime was formed exactly as for p-methyl benzophenone. M.P. after repeated recrystallization = 130° (Smith [108] gives 142°).

p-Isopropyl Benzophenone Ketimine.

Preparation of Isopropyl Benzene or Cumene.

The method used is described by Vogel [120]. The quantities however were different and isopropyl chloride was used instead of n propyl chloride. The 4-necked flask was fitted with stirrer, condenser, dropping funnel and thermometer well. The top of the condenser carried a rubber tube leading to an inverted funnel which was dipping into a beaker of water.

Into the flask was placed 117g (133ml) of dry benzene and 4g of anhydrous aluminium chloride. The stirrer was then set into motion. To the dropping funnel was now added 50g (57ml) of benzene and 17 grams of isopropyl chloride which had been dried over calcium chloride. The flask was placed in

a heating mantle and the temperature raised to 80°. The benzene-isopropyl chloride mixture was now added dropwise over a period of one hour. Stirring and heating were continued for 10 minutes longer. The increase of weight in the beaker of water, due to the absorption of hydrogen chloride, was 8 grams.

The reaction mixture was now poured onto 300g of crushed ice in a 1 litre bolthead flask and the upper layer of benzene separated. This was now washed 3 times with 50cc of 10% sodium hydroxide solution and twice with 50cc of water and dried over anhydrous magnesium sulphate.

Four such preparations were carried out and they were all fractionally distilled together with a 16" fractionating column.

Obtained: 50g of compound boiling at 152°.

Preparation of p-Bromocumene.

Into the 4-necked flask was placed 6.5g of iodine and to this was added 0.42 moles (50g) of cumene. The apparatus was set up as in the case of p-ethyl bromobenzene, with 0.42 moles (67.5g) of bromine in the dropping funnel. The experiment was now conducted as in the case of p-ethyl bromobenzene to the point where the reaction mixture was washed with water. It was now steam-distilled for 2 hours until no further product came over.

It was now left standing overnight with magnesium sulphate to dry and then fractionally distilled. Obtained: 55g boiling at 213 - 214° at 743mm pressure. $n^{13°} = 1.5406$.

Preparation of p-Isopropyl Benzophenone Imine Hydrochloride.

Into the flask was placed 0.175 mole (35g) of p-bromo-cumene, 0.2 mole (5g) of magnesium and 20ml of ether. In the dropping funnel was placed 0.14 mole (14.5g) of benzonitrile and 65ml of ether. The experiment was now carried out in a manner identical with that described for benzophenone imine. In this case the imine was not separated from the dried ethereal solution by distillation, but the hydrochloride salt was formed directly by bubbling hydrogen

chloride through the solution. The white salt was recrystallized six times from chloroform and washed each time with ether. Melting Point: 260°. (Found: Cl, 13.55; N, 5.44; Calc. for $C_{16}H_{18}NCl$: Cl, 13.66; N, 5.40%).

Formation of Ketone By Hydrolysis.

This was carried out by the same method as that followed for p-ethyl benzophenone.

Obtained: a pale yellow oil B.P. 338 - 340° at 774mm, 186 - 188° at 10mm $n^{16°} = 1.5852$.

Smith [108] gives 343° at 736mm.

Klages and Allendorf [61] give 334 - 336° at 760mm, 203 - 204° at 20mm.

Oxime.

The preparation details were the same as those for p-methyl benzophenone oxime. Obtained: a white salt which after repeated recrystallization from alcohol, gave a melting point of 130°. (Smith [108] gives 132°)

p-Tertiary Butyl Benzophenone Ketimine.

Preparation of Tert.Butyl Benzene.

The method used was that described by Huston, Fox and Binder [1]. Into the 4-necked flask was placed 130g (148cc) of dry benzene and 23g of anhydrous aluminium chloride. The flask was then equipped with stirrer, long mercury well and dropping funnel, into which was placed 25g of dry* tertiary butyl alcohol. The stirrer was set into action and the alcohol added dropwise over a period of ¾ hour, stirring being continued for 15 minutes after this addition period to ensure complete reaction. The reaction flask was placed in an ice-water bath

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* The tert.butyl alcohol was dried by adding 50g potassium carbonate to about 250cc alcohol and standing overnight. This was then filtered, 100g more of anhydrous potassium carbonate added and the flask shaken for one hour. It was then filtered and barium oxide added. This was left standing for 1½ hours with occasional shaking. After this, it was filtered and fractionally distilled, the fraction boiling at 80 - 81° being collected.

and the temperature was controlled not to rise above 40°. During the reaction, hydrogen chloride fumes were evolved and the mixture turned a deep red colour.

This mixture was then left standing overnight and decomposed by pouring on a mixture of 200 - 300g of ice and about 50 - 75ml of concentrated hydrochloric acid. The mixture was shaken until a clear yellow layer of hydrocarbon formed on top; this was then separated and left standing over magnesium sulphate to dry.

Four such preparations were carried out and the total yield of dry, impure hydrocarbon fractionally distilled. The yield was 72g of tert.-butyl benzene. B.P. 165 - 170° at 743mm $n^{12°} = 1.4970$.

p-Bromo tert.-Butyl Benzene.

0.54 moles (7.2g) of tert.-butyl benzene and 1g iron powder were placed in the four necked flask having stirrer, condenser, and calcium chloride tube, thermometer well and dropping funnel attached. The stirrer was then set into motion. Into the dropping funnel was now placed 100g of bromine and after the stirrer had been rotating for 5 minutes, addition of the halogen was begun dropwise and lasted 1 hour. Stirring was continued for 3 hours longer and then left standing overnight.

After this, it was washed with 100ml of 50% sodium sulphite and 2 lots of 100ml 5% sodium carbonate and 50ml of 10% sodium hydroxide solutions, the colour at this stage being a pale yellow. It was then dried over calcium chloride and fractionally distilled. Collected: 60g of colourless liquid having B.P. 230 - 232° at 744mm $n^{20°} = 1.5390$ (Beodthier [6] gives B.P. 232 - 233° amd Marvel, (Mueller Himel and Kaplan [74] report 230°)

p-Tert.-Butyl Benzophenone Imine Hydrochloride.

The preparation details were the same as those for p-iso-propyl benzophenone, the quantities used being 0.18 mole (38.3g) p-bromo-t-butyl benzene, 0.2 mole (5g) magnesium and 30ml of ether in the reaction flask. After

the formation of the Grignard reagent, a mixture of 0.16 mole (16.5ml) of benzonitrile and 60ml of ether was added dropwise.

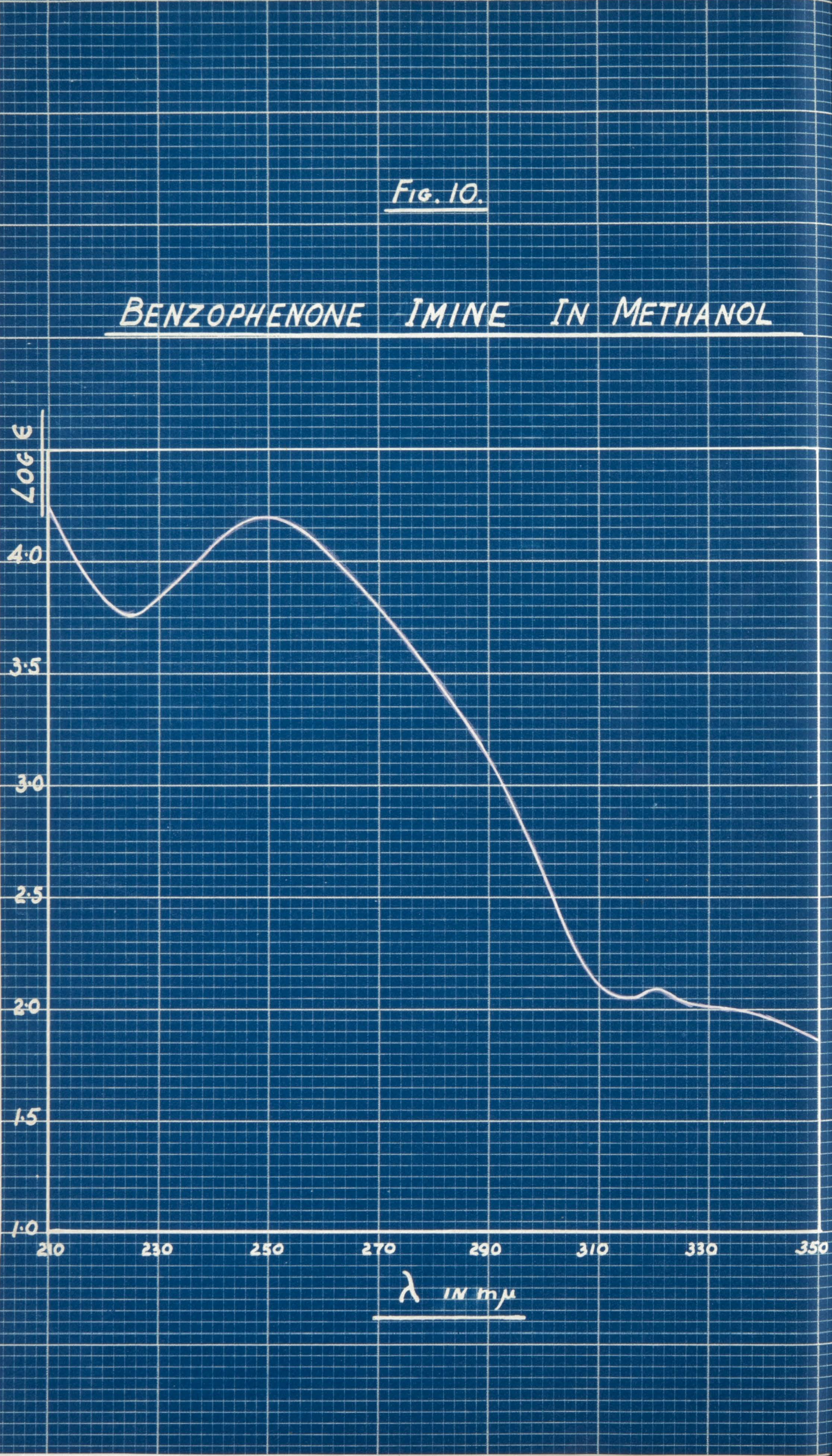
The imine was not separated, but the hydrochloride was formed directly by precipitating from ethereal solutions. This, after several recrystallizations from chloroform, gave a white salt which sublimed considerably between 250 - 280° and melted at 280 - 282°. (Found: Cl, 12.88; N, 5.15. Calc. for $C_{17}H_{20}NCl$: Cl, 12.96; N, 5.13%).

p-Tert.-Butyl Benzophenone.

This was formed by the hydrolysis of the ketimine hydrochloride with 6N hydrochloric acid as described for p-ethyl benzophenone. Obtained a pale yellow viscous oil. This was distilled 3 times under vacuum and collected fraction boiling at 198° at 13mm. $n^{19°}$ = 1.5762. (Found: by Dr. Campbell of Otago University H, 7.86; C, 85.86; Calc. for $C_{17}H_{18}O$: H, 7.56; C, 85.70%).

FIG. 10.

BENZOPHENONE IMINE IN METHANOL



CHAPTER VI

RESULTS AND DISCUSSION

By examining the spectra of benzophenone and benzophenone imine the marked similarity between the two can be observed. They each have a strong absorption band in the 2500Å region, and a minimum in the 2300Å region. It is also surprising to note that the very weak peak in the 3300Å region, which has been described as typical of the N $\longrightarrow$ A transition of a carbonyl group connected to a conjugated system, is also present in benzophenone imine. Ley and Wingchen (67) explained this on the grounds that the =O atom and the =NH group both have the same number of valence electrons, and hence lead to the same λ max and ϵ max of absorption. This does not however agree with the arguments put forward by Lewis and Calvin (65), nor does it agree with the results obtained for Fenchone (see APPENDIX). The following table lists the different results obtained for benzophenone and benzophenone imine by the present author, and by others who have studied them.

Benzophenone

	λ max in Å.	logϵ	λ max in Å.	logϵ	λ max in Å.	logϵ
Present Author			2520	4.24		
Ley and Wingchen	1900	4.7	2520	4.30	3300	2.25
Meisenheimer & Dorner (76)			2500	4.25	3300	2.25
Szmant and McGinnis (112)			2530	4.27		

Benzophenone Imine

	λmax in Å.	logϵmax	λ max in Å.	logϵ max
Present Author	2500	4.20	3220	2.08
Meisenheimer & Dorner	2520	4.20	3320	2.20

In a paper published on hydroxy-aldehydes and ketones,

FIG. II.

KETONES IN METHANOL

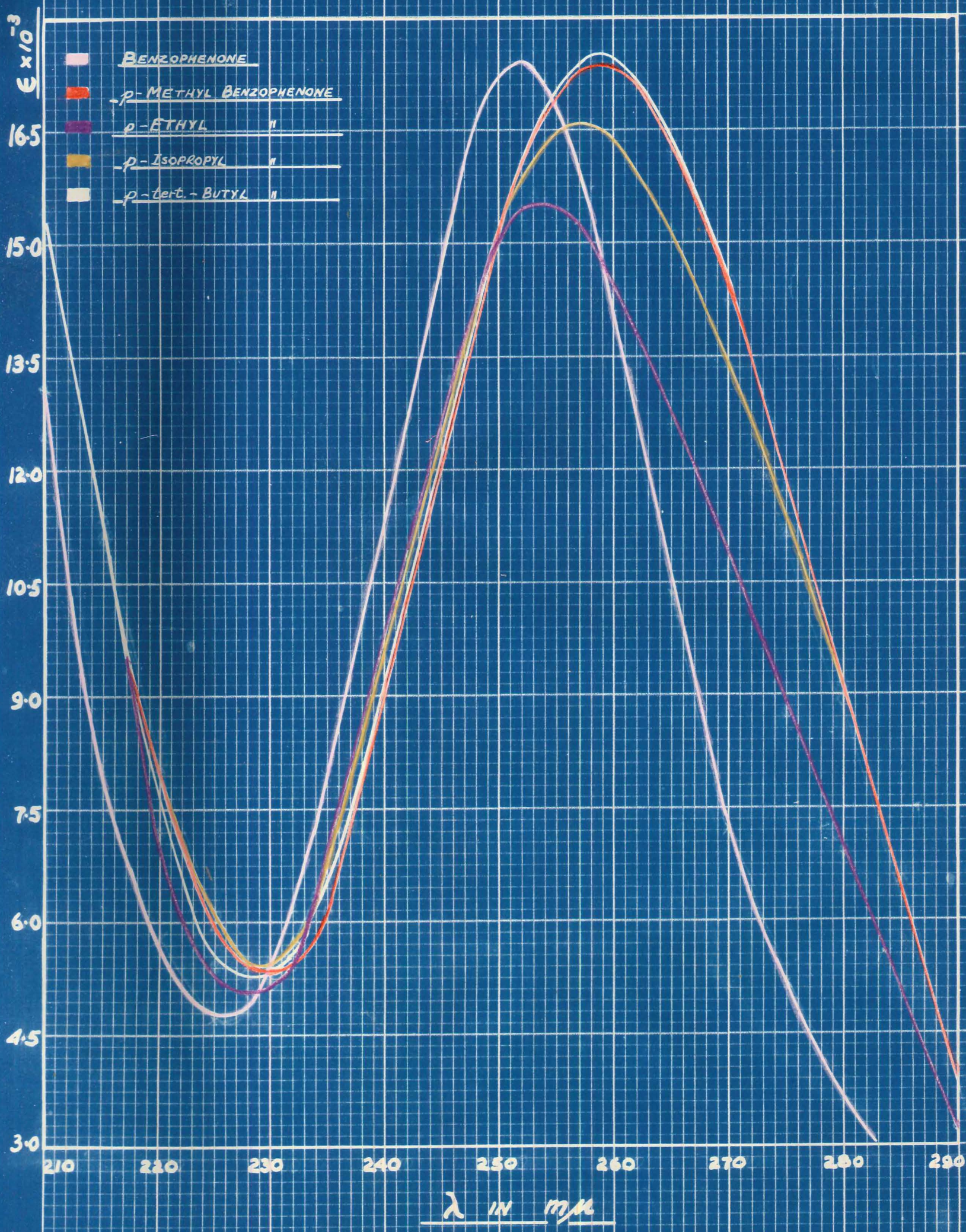
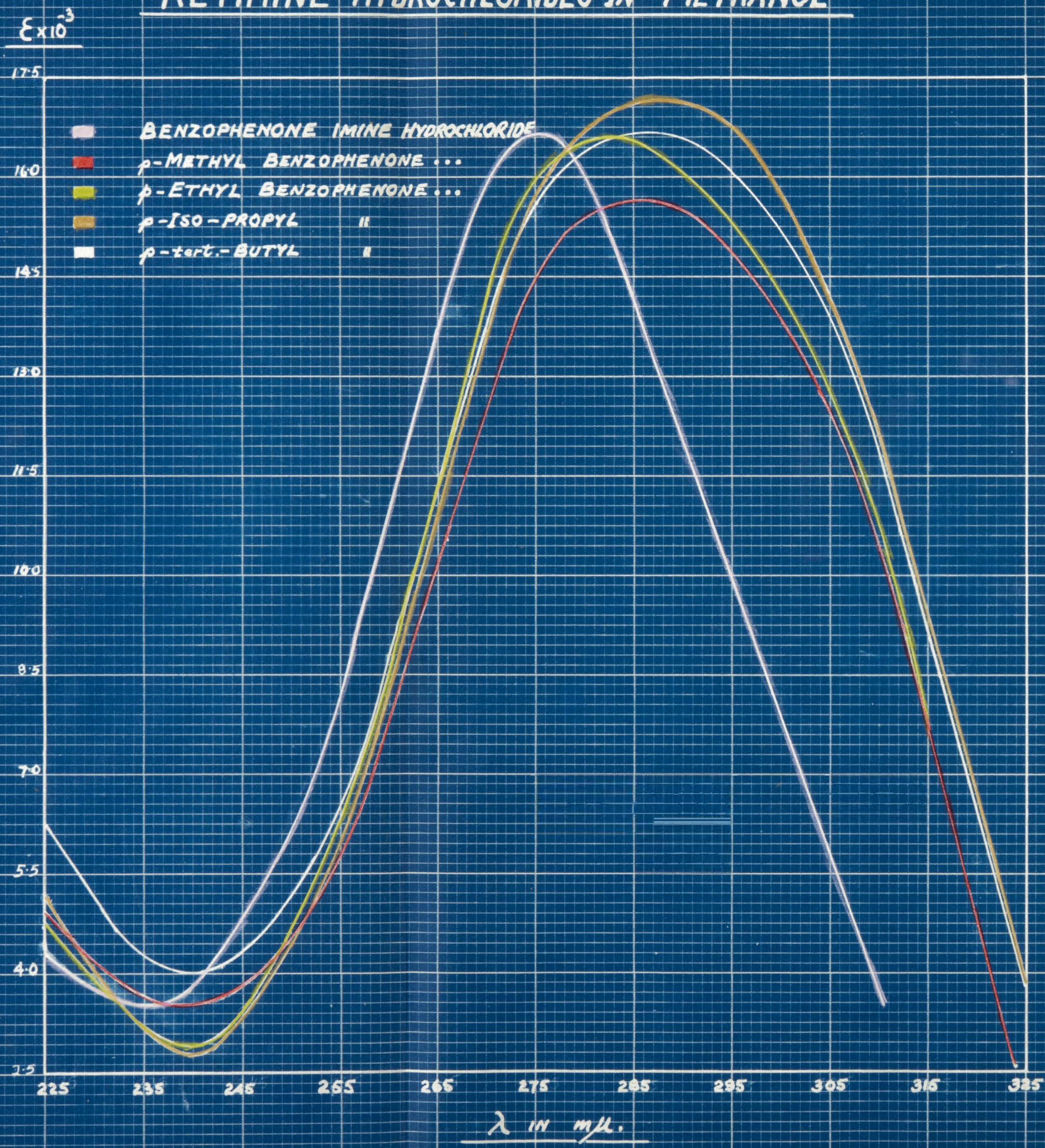


FIG. 12.

KETIMINE HYDROCHLORIDES IN METHANOL



Morton and Stubbs [83] claim that the absorption in the 2500A region is characteristic of benzenoid absorption, while that in the vicinity of 3000Å is due to the carbonyl group. Evans and Gillan [35], giving data for a series of unsaturated aldehydes and ketones, and for a parallel series of semicarbazones of the carbonyl group having the general structure C=C-C=O and C=C-C=N, show that the λ max for a band of crotonahldehyde at 2170Å moves toward the red by increasing the size of the chain. Hence it is equally possible for the increase in conjugation to result in a shift of λ max from Ca 1900Å to 2500Å for an N $\longrightarrow$ V transition in the carbonyl group.

In the present work, the stress has been laid more on finding the effects due to substitution rather than obtaining an absorption curve over a wide range of wave-length measurements. This has resulted in a concentration on the 2500Å region where the curve is sharp and of high extinction, in contrast to the broad curve of very low intensity found in the longer wave-length region. This latter curve was very difficult to read on the spectrophotometer, and the accuracy was lowered due to the necessity of using a relatively concentrated solution, and long absorption cell.

The data obtained for the ketones is given below.

	Benzophenone	p-Me-	p-Et-	p-isoProp-	p-tert.Butyl
λ max in Å	2520	2590	2535	2570	2585
ϵ max	1.750	1.745	1.555	1.660	1.755

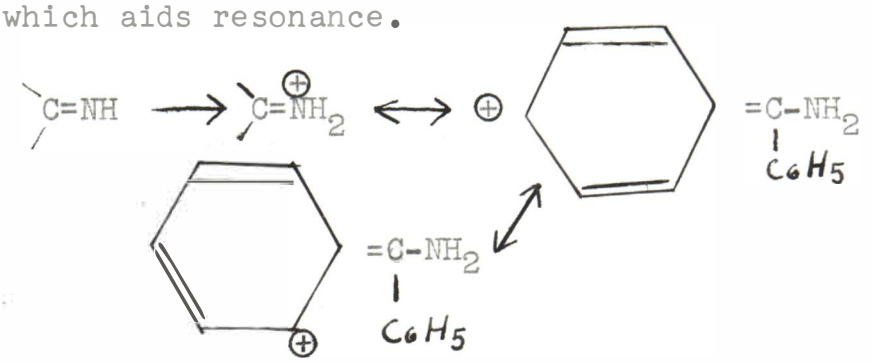
These figures correspond to the graphs in Figure II.

The ketimines were converted to the hydrochloride salt because of the greater ease with which these salts could be handled. The following are the data obtained.

	Benzophenone Imine Hydrochloride	p-Me-	p-Et-	p-isoProp-	p-tert.Butyl
λ max in Å	2755	2855	2820	2875	2875
ϵ max	1.665	1.570	1.660	1.715	1.680

It can be seen that the absorption peak has been moved

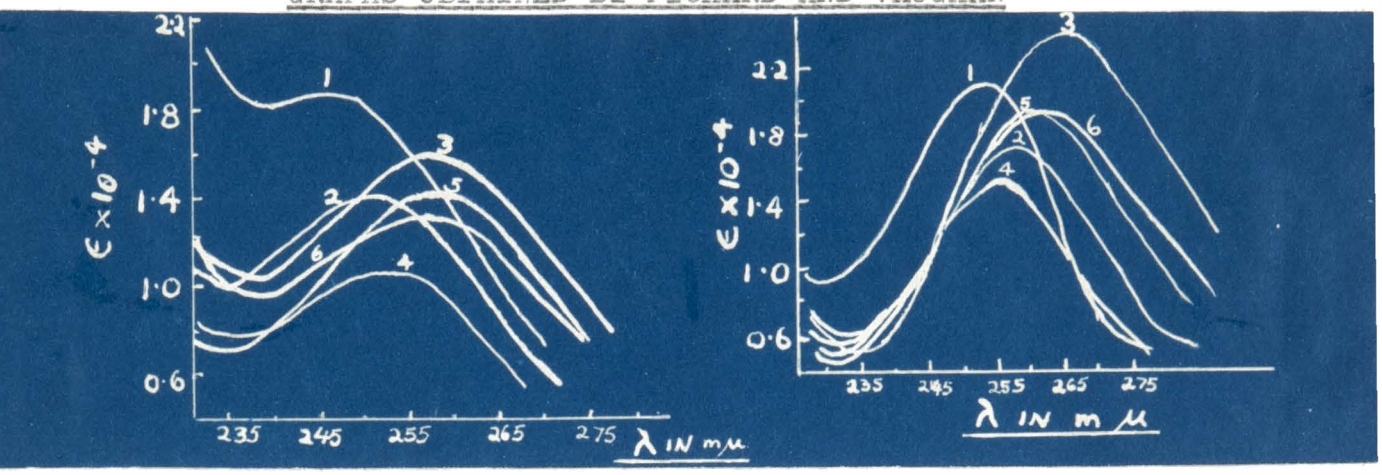
an average of 250A from that which existed in the imine base. This is to be expected, from the fact that by the introduction of the HCl group an increase in conic structures result which aids resonance.



On these lines, it is surprising to note that Culbertson (33) who has recently published a paper on factors affecting the rate of hydrolysis of ketimines through a study of their hydrochloride salts, gives the λ max of benzophenone imine hydrochloride as 2500Å, while the extinction coefficients is 15,000. Another surprising result that Culbertson gives is that while admitting that steric hindrance can take place in 2-methyl benzophenone imine hydrochloride, he finds that this compound has a λ max at 2750Å, while the 4-methyl compound has an absorption maximum at 2600Å. Culbertson claims that the 2-methyl compound could not display resonance or tautomerism, yet he fails to give the reason for this long shift in λ max. It is usually found that in benzene rings connected directly, as in biphenyls, or through a short chain, the coplanarity is destroyed by steric hindrance thus reducing comjugation and so shifting the wave-length of absorption toward the far ultra violet (37, 58). Further, a methyl group in the para position would have greater power to increase conjugation than would a similar group in the ortho position, since it is acting through a longer chain. The work published by Pickard and Vaughan (93) show direct contrast to that of Culbertson. The former workers have published results for a series of O; p- and m- ditolyl ketones and ketimines.

Figure 13

GRAPHS OBTAINED BY PICKARD AND VAUGHAN



Ketimines Ketones

1=di-o-tolyl-, 2=di-m-tolyl-, 3=d-p-tolyl-

4=o-tolyl-m-tolyl, 5=o-tolyl-p-tolyl, 6=m-tolyl-p-tolyl.

The results for the ortho and para compounds being:

	max ketone	max ketimine
Di-o-tolyl	2520Å	2470Å
Di-p-tolyl	2640Å	2580Å

Another discrepancy which is noted in Culbertson's work is the position of λ min. Whereas in Pickard and Vaughan's results as well as those obtained in the present work, the minima lie within 50 or 60A of each other, those of Culbertson's vary over a wide range of wave-lengths. A possible explanation of these differences is that Culbertson's results were obtained with the help of other workers; it is thus possible that some considerable time elapsed between the preparation of the ketimines and their use in the spectrophotometer. The time factor is often very important in dealing with absorption spectroscopy, especially with these unstable compounds.

Hyperconjugation.

The trend which the spectra studied in this work follow, appears to be such as to confirm the hypothesis of hyper-conjugation, a discussion of which follows.

The effect was first noticed by Baker and Nathan in 1935, when studying the rate of reaction of various alkyl-substituted benzyl bromides with pyridine. It was found that all alkyl substituents increased the reaction rate, while with a single p-alkyl substituent the effect decreased

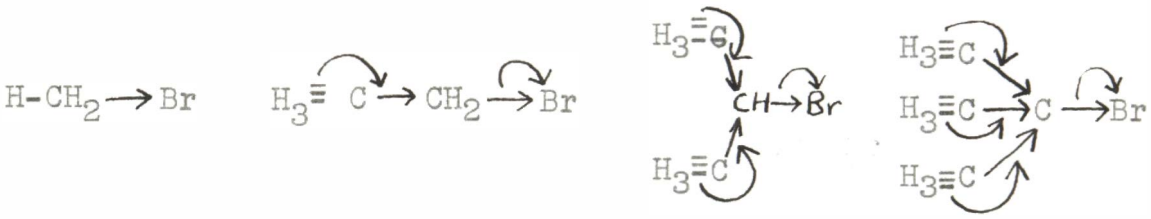
in the order

Me > Et > i-Pr ~ t-Bu

If the reaction rate were to increase with alkyl substitution by charge transfer through the process of induction, then the order should be reversed.

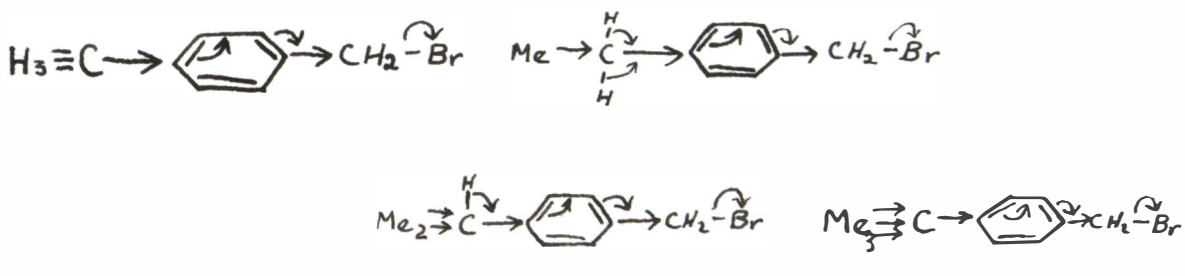
It has been observed through hydrolysis experiments (3), as well as those involving ionization potentials (32) that hypercomjugation is of greater importance in a conjugated system than in a short chain system or in an insulated system (where conjugation has been destroyed).

Taking ionization of halides as an example of the relative importance, we have in the simple alkyl series



+I effect minimum	increasing →	maximum
+T effect minimum	increasing →	maximum

i.e. the tautomeric effect reinforces the inductive effect both absoutely and differentially as between one alkyl group and another. In the p-alkylbenzyl bromides, however, the trend is



+I effect minimum	increasing →	maximum
+T effect maximum	decreasing →	minimum

i.e. in this series, the tautomeric effect reinforces the general inductive effect absolutely but opposed it differentially as between one alkyl group and another.

Conjugation causes (a) the unoccupied M.O. to become less strongly antibonding, and (b) a raising of the ground state of the occupied bonding M.O.; and hence absorption occurs at longer wave-lengths; an effect which increases with progressive conjugation. A substituted methyl group tends to increase this conjugation effect and so was first

called hyperconjugation by Mulliken, Reike and Brown [89].

The above authors have attempted a M.O. approach to the whole question of hyperconjugation. They consider, as a basic principle, that the difference in conjugative power of $-C{\equiv}H_3$, $-C{\equiv}N$ and $-C{\equiv}CH$ are quantitative rather than qualitative in character. Conjugation in general was classified as follows,

$HC{\equiv}C-C{\equiv}CH$
$N{\equiv}C-C{\equiv}N$) first order conjugation

$H_3C{\equiv}C-C{\equiv}CH$) Second order conjugation;
$H_3C{\equiv}C-C{\equiv}N$) first order hyperconjugation

$H_3{\equiv}C-C{\equiv}H_3$ third order conjugation; second order hyperconjugation.

The most important case and the one to which the general term hyperconjugation is used is that of second order conjugation. Calculations made by Mulliken, Reike and Brown show that the hyperconjugation energy of a CH_3 or CH_2 group is very nearly the same when bonded with an unconjugated C=C bond, as with a conjugated C=C bond system, or with (resonating) C=C bonds such as toluene. They point out that acceptor bonds in first order hyperconjugation, $H-\overset{\curvearrowright}{C}-C=\overset{\curvearrowright}{C}$, are very appreciably strengthened and shortened, whereas the donor bonds are not appreciably affected.

Coulson[29a] has attempted an explanation of this phenomenon from a M.O. point of view. He assumes that three of the hydrogen atoms lying in one plane combine to form a molecular orbital which is described by the group wave function,

$$\psi(Ha) + \psi(Hb) + \psi(Hc).$$

This symmetric orbital is destroyed during hyperconjugation, with the result that two new orbitals are formed having a wave function

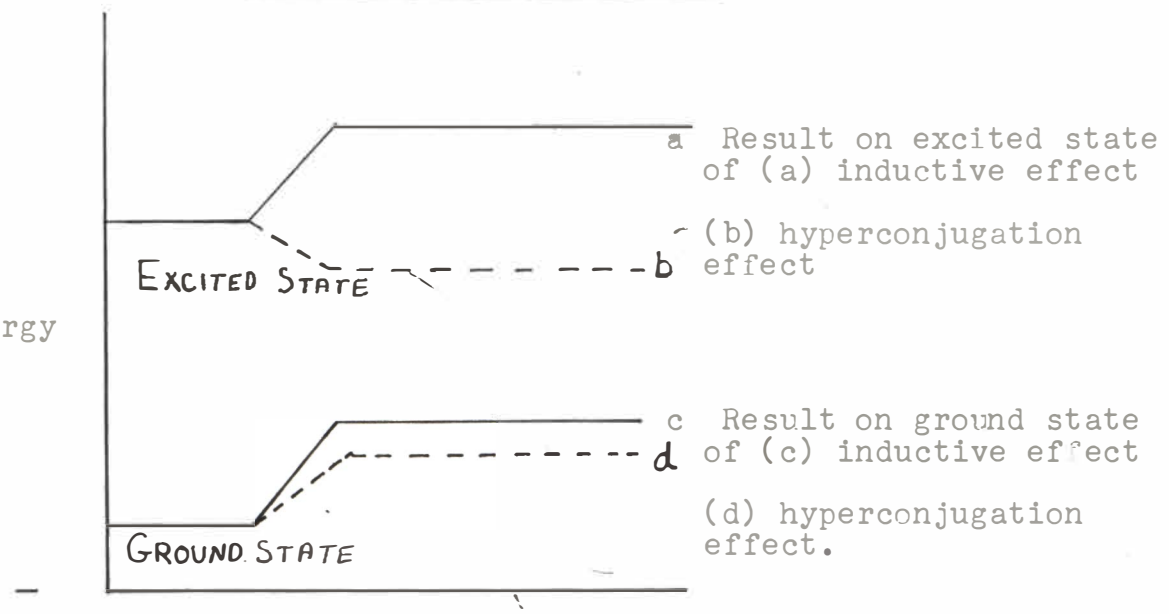
$$\psi(Ha) - \tfrac{1}{2}\left[\psi(Hb) + \psi(Hc)\right]$$

with a nodal line separating them. These new orbitals formed are similar to a π-type orbital. It is therefore possible to think of the H_3 group as being represented by a pseudo-atom, with a orbital that could conjugate with the benzene ring (see reference 29a for diagrams).

Walsh (123) has suggested that, in the substitution of a hydrogen atom by a methyl group, the hybridization is changed so that in the system $H_3\equiv C-\overset{1}{C}=C\overset{2}{<}$, the C-C bond assumes more S character thus leaving more p character in the C=C bond. This increase of π bonding tends to delocalise the system, so that the π electrons are held more loosely and are more easily removed. This phenomenon has been described by Walsh as being due to the inductive effect, and results in a raising of the ground state orbital, as regards the excited state, computations show that the inductive effect results in a raising of this level, the change in the excited, however, being smaller than that brought about in the ground state

Figure 14

RESULTS OF HYPERCONJUGATION AND THE INDUCTIVE EFFECT ON THE GROUND AND EXCITED STATES



Hyperconjugation of the CH_3 group with the above system not only raises the ground state but also causes a decrease in the excited state.

Hyperconjugation and the inductive effect are therefore opposed in the excited states, and the importance of hyperconjugation can only be found after allowance has been made of the role that charge transfer plays.

The only data so far available on alkylation of the benzene ring with respect to absorption in the ultra violet, have been by Matsen, Robertson and Chouke (75). These authors have plotted the wave-lengths of the 0,0 bands for

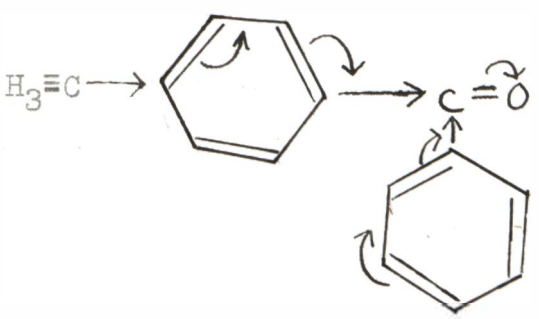
for the spectra of toluene, ethyl-, isopropyl-, and tert.-butyl benzene in both the vapour state and benzene. (The 0,0 bands are those which arise from electron transition from the lowest vibrational level of the ground state to the lowest vibrational level of the first excited state). The positions of the 0,0 bands and their extinction coefficients in alkylbenzenes in solution have been estimated by the present author from the curves published by Matsen, Robertson and Chouke, and are as follows:

R in PhR =	H	Me	Et	i-Pr	t-Bu
0,0 band =	2640	2687	2680	2675	2671
K_{max} =	100	225	182	164	155

The largest shift occurs in toluene, and the displacement decreases in the series ethyl-, isopropyl, and tert.-butyl-benzene, being smallest in the last named. The hyperconjugation must swamp the inductive effects of the alkyl groups which, by itself, causes wave-length shifts and intensity increases in the reverse order,

t-Bu > i-Pr > Et > Me .

From the preceeding discussion on hyperconjugation, it can be seen that this factor plays an important part in the interpretation of the results obtained in this investigation. The tautomeric effect produced by the methyl group can be illustrated as being similar in type to that of the benzyl bromides on page 75 .



The results obtained for the ketones and the ketimine salts are not however identical. In the former, the methyl-compound has the longest wave-length of absorption, but the order is not the same as the results of Matsen, Robertson and Chouke. It appears that although hyperconjugation may be more important in the ketones, the inductive

effect is also a large factor.

Figure 15a

PLOT OF KETONES AGAINST WAVE-LENGTH

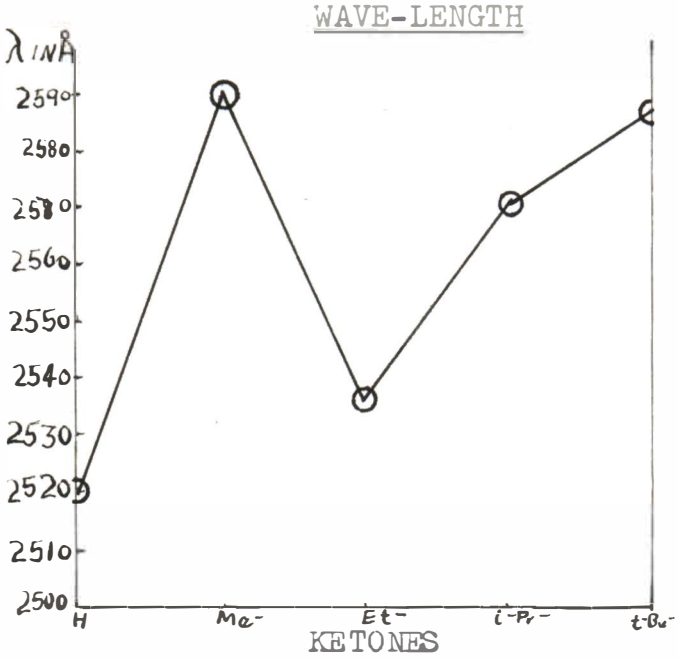
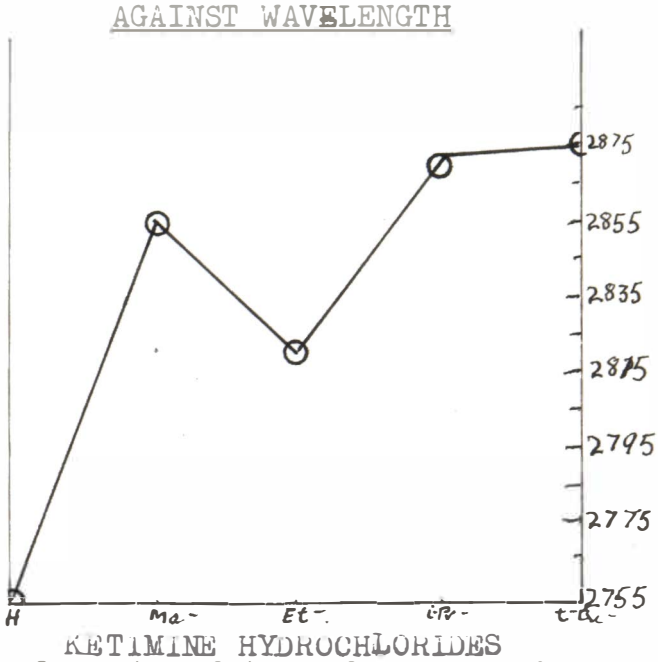


Figure 15b

PLOT OF KETIMINE SALTS AGAINST WAVELENGTH



Since the results do not show a clear trend toward hyperconjugation, as in the work of Matsen, Robertson and Chouke, it is probably safer to say that the two effects present are of near or equal value. In any case one cannot postulate with any degree of accuracy which will be the most important. This can be seen from the fact that in the ketone compounds, the p-methyl displays greater absorption (by5Å), while in the ketimine salts both the p-tert.-butyl and p-iso-propyl compounds show and equal λ max which is 20Å greater than that of the p-methyl compound. The p-ethyl compound however, displayed a lower bathochromic shift than the other substituents.

A possible explanation for this may be given on the basis of Walsh's theory [123] (page 77), dealing with the raising and lowering of ground and excited states. In the methyl group the hyperconjugation effect is far greater than the inductive effect, and hence the excited state will be lowered while the ground state is raised. In iso-propyl and tert.-butyl, charge transfer plays a greater part, hence raising the ground state. In the ethyl group, however, neither hyperconjugation nor the inductive effect are very active; hence no great shift in λ max results.

CONCLUSION

The problem of instability of the ketimines is still unsolved. Although it appears that steric hindrance plays a big part in decreasing the rate of hydrolysis, this is not a general case. Pickard and Vaughan, for example, state that tert.-butyl p-tolyl ketimine could not be hydrolysed even when refluxed for 48 hours with 6N hydrochloric acid. On the other hand, di-o-tolyl ketimine, which would be expected to be equally sterically hindered, was hydrolysed with a rate equal to that of di-p-tolyl ketimine.

The question of the dialkyl ketimines is also an unsolved problem. It is strange that alkyl aldimines have been prepared, and yet attempts to prepare the dialkyl ketimines have failed. It should be possible, however, to prepare such ketimines if sufficient care is taken, through the use of one of the methods which does not entail a high temperature, and in which moisture is excluded. It may be possible to prepare the ketimines directly from the aldimines by use of diazomethane as in the Buchner-Curtius-Schlotterbek reaction. However, to the knowledge of the present author, this method has not been attempted.

The diaryl ketimines have absorption spectra which do not differ greatly from those of their related ketones. The absorption of the basic carbonyl and imino groups as found in fenchone however, show a marked difference.

Hyperconjugation is an important effect both in the ketones and ketimines. From the data obtained, however, it would appear that it is of greater importance in the ketones than in the ketimine hydrochlorides. This can also be seen from the work of Pickard and Vaughan [93] on ketones and ketimines.

APPENDIX

THE FENCHONE SERIES

Purification of Fenchone.

Commercial fenchone was purified, for use in the spectrophotometer, by distillation at atmospheric pressure. The substance was distilled twice and the fraction boiling at 188° collected and used, its refractive index $N^{18°} = 1.4635$ (Heilbron [46] gives B.P.=193.5° and $n^{20°} = 1.4623$).

Preparation of Fenchone Oxime.

The method is similar to that used by Rimmini [99]. To a solution of 10 grams of hydroxylamine dissolved in 50cc of alcohol, 20 grams of sodium hydroxide (commercial) was added. To this was then added 10 grams of Fenchone and the mixture refluxed gently for 10 hours in a 150ml flask. 5 grams of hydroxylamine were then added and refluxing continued for 2½ hours longer. At the end of this period, 2½ grams of hydroxylamine and 2½ grams of sodium hydroxide were added and refluxing continued for a further period of 3 hours.

Most of the alcohol was now evaporated and 100cc of ice-cold water rapidly added to the flask with continuous stirring. White crystals of fenchone oxime precipitated, being easily filtered at the pump through a Buchner funnel. 9 grams of oxime melting at 120° was obtained as the crude yield. This was recrystallized three times from petroleum ether (boiling range 40 - 60°) giving a melting point 161 - 162° (Beilstein [4] 163°, Heilbron [46] 158 - 159°, Simonsen [106] 164 - 165°).

Preparation of Fenchone Imine.

A solution of 4½ grams of fenchone oxime in 75cc of ether was made in a 250cc conical flask. Nitrous acid was then made by dissolving 4½ grams of sodium nitrite in 10cc of ice-cold water; to this was then added very slowly 10cc of hydrochloric acid made by diluting concentrated acid in ratio 2 volumes of water to 1 volume of acid. The glass

vessels were kept in an ice-salt bath during addition to prevent decomposition of the acid. The nitrous acid solution was then added to the oxime solution; reaction took place immediately and a white precipitate was formed which dissolved immediately on shaking the flask. Two layers then appeared, the solution slowly turning yellow and finally a light red. Further shaking did not change the colour. The ethereal layer was then separated and, on evaporation, gave 3 grams of a golden coloured salt melting at 55°, On recrystallization, a white salt M.P. 57 - 58° was obtained. This was the salt known as fenchonenitrimine.

To the nitrimine was slowly added 80cc of 25% ammonia solution with continuous shaking. This was then heated in a water bath (90°) for 10 minutes. The flask was then cooled in ice, forming a dispersion of oil in aqueous solution. The oil was then separated by centrifuging and dissolved in 20cc of ether. Potassium hydroxide pellets (as dehydrating agent) were added to the solution and left standing for 1½ hours. The ether was then distilled off at atmospheric pressure and the oil distilled twice under reduced pressure. The product was a colourless oil B.P. 78 - 79° at 14mm $n^{17°}$ = 1.477 (Mahla [72] gives B.P. 83° at 15mm $n^{17°}$ = 1.478).

The molecular weight was determined by lowering of freezing point of benzene.

Experimental: 148.5, Calc. for $C_{10}H_{17}N$: 151.

Spectroscopic Results and Discussion.

The absorption measurements of fenchone and fenchone imine, can be taken as being due to that of the carbonyl and imino groups only. The remaining hydrocarbon ring to which these groups are attached have very little influence, either bathochromic or hypsochromic. In both these compounds the molecular extinction coefficient ϵ max is very low. The plot of fenchone appears to have three small peaks in the near ultra violet region, the major one being at

FIG. 16.

FENCHONE IN METHANOL

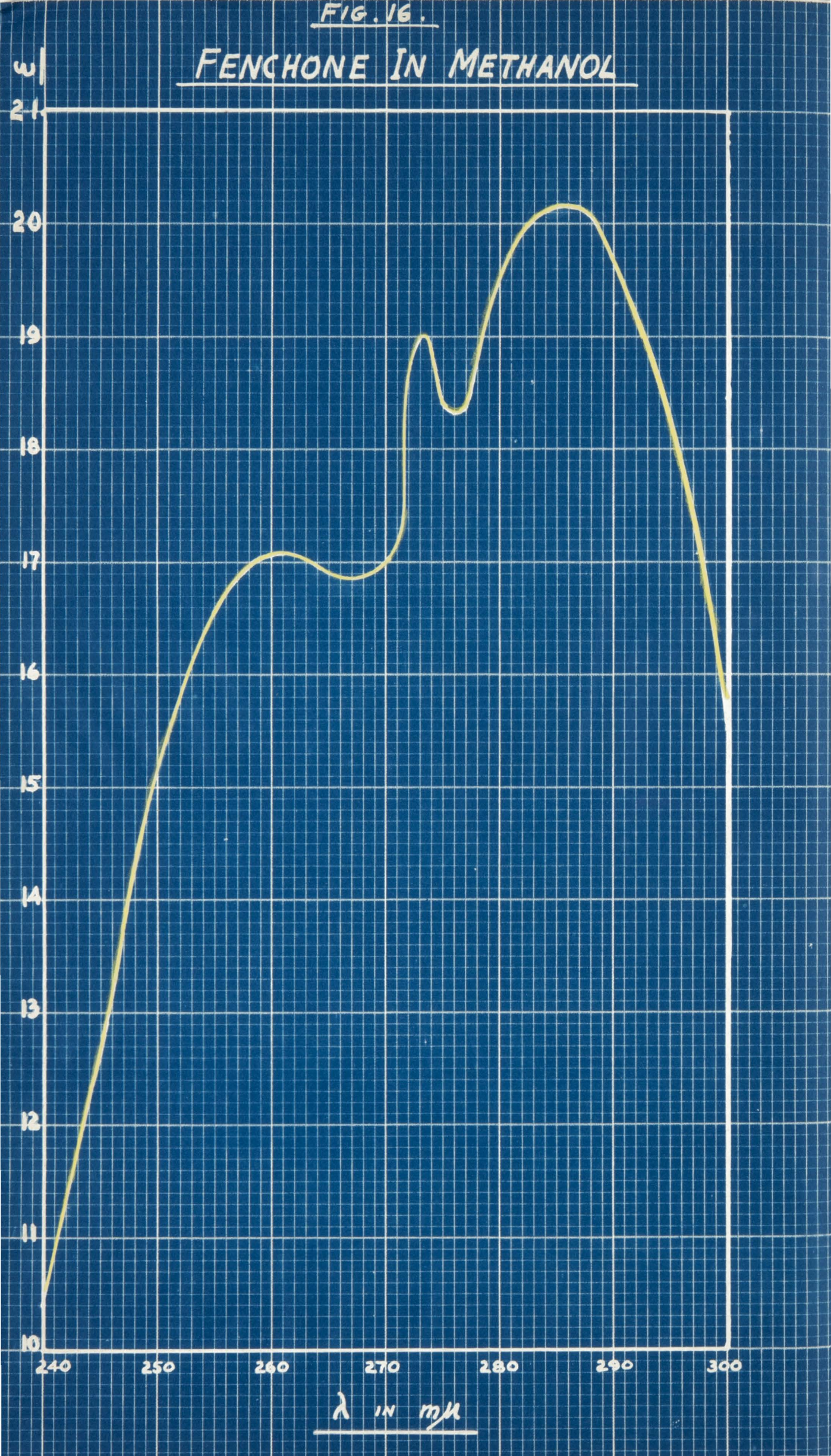
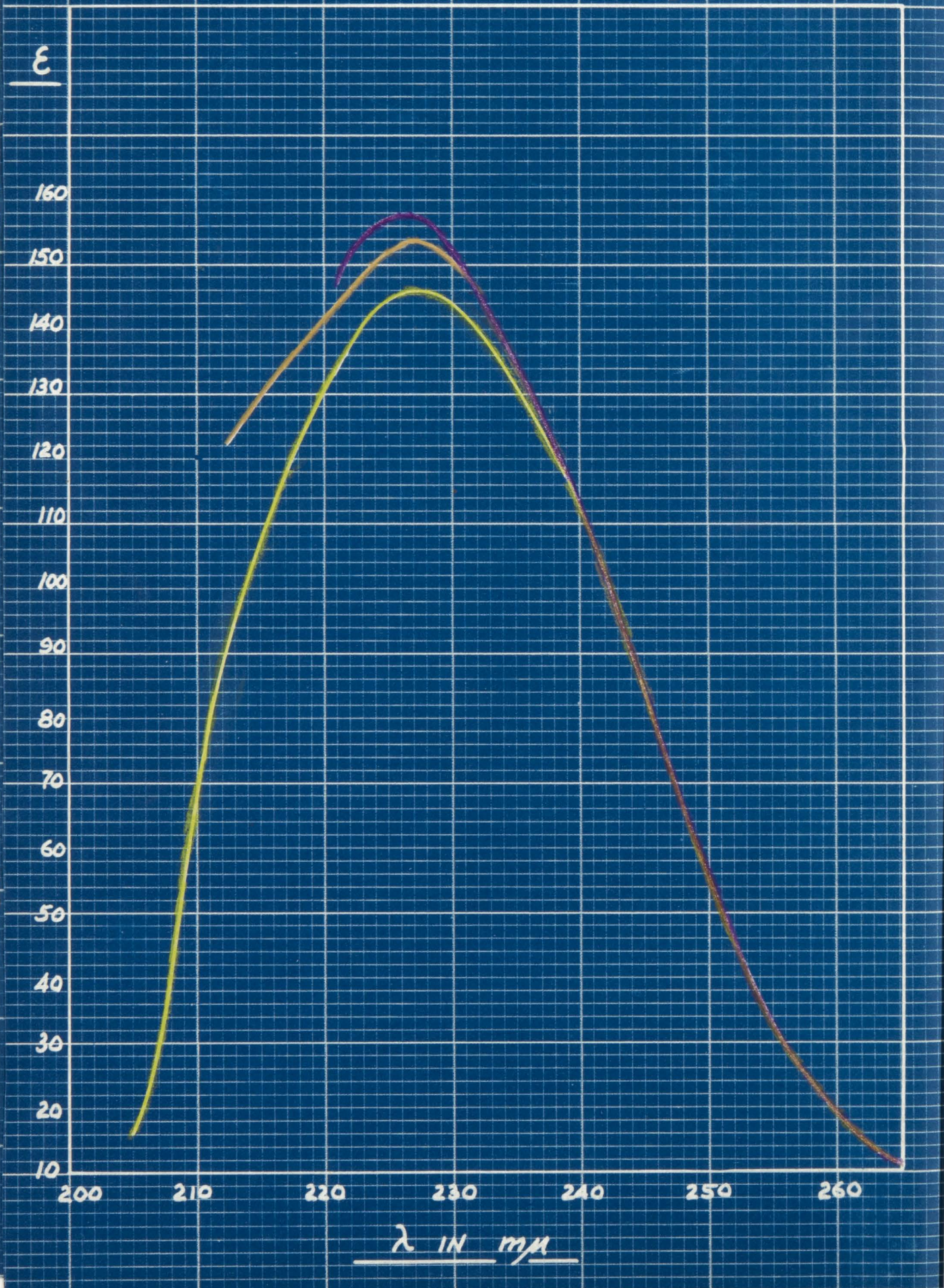


FIG. 17.

FENCHONE IMIME IN METHANOL

$c = 1.02 \times 10^{-2}$ m/l, $l = 1.0$ cm
$c = 1.02 \times 10^{-2}$ m/l, $l = 0.5$ cm
} UVISPEC

$c = 1.02 \times 10^{-2}$ m/l, $l = 1.0$ cm MEDIUM QUARTZ SPECTROPHOTOMETER



2860Å and having an ϵ max of 20. This agrees closely with the data on acetone, acetaldehyde, and other simple carbonyl systems (13a) which have an absorption curve ranging from 2750Å to 2900Å, with ϵ max equal to ca.20.

Fenchone-imine has a λ max at 2260Å - 2270Å, and its extinction coefficient is higher (ca. 150) than fenchone (see figures 16 and 17). This agrees well with the postulate of Lewis and Calvin (65) (see also page 29) but cannot however be explained in terms of the absorption data taken for benzophenone-imine. At the present time, no data exist on the absorption by the simple =NH group, hence no comparison can be given with the work of other experimentors. The present author cannot offer any explanation as to the electronic transitions which may take place in the molecule.

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